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No. 1.

THE COMPOSITION OF SOME MINE GASES, AND A DESCRIPTION OF A SIMPLE METHANE APPARATUS.*

By G. A. BURRELL.†

The Bureau of Mines has in the study it has been making of mine gases, examined samples taken under different conditions, some of which are here presented; also some analytical results obtained in related experimental work.

NO. 1 SERIES.

NO. 1 SAMPLE: INCOMPLETE COMBUSTION OF METHANE. ORIGINAL MIXTURE CONTAINED 10.03 PER CENT CH₄

Products found after explosion.....	10.16% CO ₂
	2.16% CO
	1.39% H ₂
	86.32% N ₂
	.00% O ₂
	.00% C ₂ H ₄

NO. 2 SAMPLE: INCOMPLETE COMBUSTION OF METHANE. ORIGINAL MIXTURE CONTAINED 10.94 PER CENT CH₄

Products found after explosion.....	8.35% CO ₂
	4.47% CO
	3.66% H ₂
	83.52% N ₂
	.00% O ₂
	.00% C ₂ H ₄

In these experiments pure methane was prepared and mixed with air in such proportion that not enough of the latter was present for the complete combustion of the methane. The mixtures were then exploded and the products of combustion examined. The most explosive proportion of methane and air contains 9.47 per cent of methane. When the latter is increased above this figure certain products are formed about which there has been some disagreement. Some investigators have gone on record as saying that no carbon monoxide is formed. According to these experiments the carbon monoxide and hydrogen increase, and the carbon dioxide decreases as the methane content of the original mixture is raised. Olefine hydrocarbons, acetylene, or unburned methane were not found in the products of combustion. The carbon monoxide and carbon dioxide formed satisfy the carbon originally present in the methane. To the carbon monoxide formed in this manner is due some of the carbon monoxide found in the after-damp following mine explosions. Not entirely, however, and in many cases

the smaller proportions is formed in this manner, because the incandescent carbon of heated coal dust appears to be mainly responsible for the production of carbon monoxide found after dust explosions.

NO. 2 SERIES.

CREVICE SAMPLES OBTAINED AFTER EXPLOSIVES HAD BEEN FIRED IN COAL MINES.

No. 1 sample.—Permissible explosive:

CO ₂	16.8%
O ₂	4.3%
CO	22.8%
CH ₄	17.3%
H ₂	8.9%
N ₂	29.9%

No. 2 sample:

CO ₂	9.1%
O ₂	7.5%
CO	3.2%
CH ₄	14.1%
H ₂	4.1%
N ₂	62.0%

No. 2 series of samples show the gases formed by firing blasting explosives in coal mines. Both black powder and permissible explosives produce noxious gases. These samples were taken from the crevices produced by the breaking down of the coal. The explosive and noxious character of the gases will be observed, and accounts for the fact that the miner is sometimes burned when he innocently puts his lamp to the coal to examine the effects of his blast.

NO. 3 SERIES.

NO. 1 SAMPLE.—CREVICE TAKEN IMMEDIATELY AFTER SHOT A HAD BEEN FIRED.

CO ₂	1.40%
O ₂	19.31%
CO	1.45%
CH ₄	1.40%
H ₂	.74%
N ₂	75.70%

NO. 2 SAMPLE.—SAMPLE TAKEN FOUR MINUTES AFTER SHOT A HAD BEEN FIRED.

CO ₂	.56%
O ₂	20.22%
CO	.16%
CH ₄	.71%
H ₂	.06%
N ₂	73.29%

NO. 3 SAMPLE.—CREVICE TAKEN IMMEDIATELY AFTER SHOT B HAD BEEN FIRED.

CO ₂	2.50%
O ₂	16.91%
CO	1.21%
CH ₄	4.88%
H ₂	1.06%
N ₂	73.44%

NO. 4 SAMPLE.—SAMPLE TAKEN FOUR MINUTES AFTER SHOT B HAD BEEN FIRED.

CO ₂	.30%
O ₂	20.61%
CO	.02%
CH ₄	.25%
H ₂	.01%
N ₂	78.81%

*Paper presented at the December meeting of the Coal Mining Institute of America, by permission of the Directors of the U. S. Bureau of Mines & Chemists, Mine Gas Investigations U. S. Bureau of Mines.

No. 3 series of samples represent further gases obtained after explosives had been fired to break down coal. The crevice samples were obtained by proceeding immediately to the face after the shot had been fired and collecting the samples as the gas exuded from the coal crevices. In each case a wait of 4 minutes was made and then the sampler proceeded to the face to collect another sample at about the place the miner would stand to attend to his shot. In one case .16 per cent of carbon monoxide was found, a harmful quantity. These explosives were fired under conditions which do not represent best practice. Other experiments are being carried on by the bureau to obtain further data on this subject, so as to determine the causes which lead to the production of harmful quantities of noxious gases. Work thus far accomplished shows that it is bad practice to proceed immediately to the face after a shot has been fired. Even those powders which contain within themselves sufficient oxygen for the complete combustion of the carbonaceous matter present in the explosive, produce when fired in coal mines, some carbon monoxide, due again to reaction with the carbon of the coal dust. Some explosives, however, are themselves very deficient in oxygen.

NO. 4 SERIES.

COMBUSTION OF GASES FROM AN INCLOSED AREA IN AN ANTHRACITE MINE.

Sample No.	Date.	Per cent.				
		CO ₂	O ₂	CO	CH ₄	N ₂
1	Oct. 31.....	2.2	15.0	.0	14.0	68.8
2	Nov. 1.....	2.3	14.6	.0	18.1	65.0
3	Nov. 2.....	2.6	6.2	.0	24.2	67.0
4	Nov. 2.....	2.9	5.7	.0	29.3	62.1
5	Nov. 3.....	2.8	4.1	.0	34.9	58.2
6	Nov. 6.....	2.6	3.0	.0	53.0	41.4

These gases, series No. 4, show the composition of the atmosphere in enclosed section of an anthracite mine. This section of the mine was sealed off because of a fire which existed in an adjoining section. The fire did not affect the particular area from which these samples were obtained because of a heavy intervening roof fall, consequently the gases represent those trapped and given off normally in a stagnant section, except that a stopping was leaking and some air was finding its way into the interior from the ventilating current. The stopping was tightened and the rapid absorption of oxygen by the coal is shown by the third analyses. Four days later the oxygen had dropped to 3 per cent. Even so, some air was finding access. The rapid accumulation of methane is also shown, 53 per cent on the sixth day.

NO. 5 SERIES.

COMPOSITION OF GASES FROM AN INCLOSED AREA IN A BITUMINOUS MINE.

Sample No.	Per cent.				
	CO ₂	O ₂	CO	CH ₄	N ₂
1.....	1.50	.30	.00	5.29	92.91
2.....	1.20	.30	.00	5.37	93.13

Series No. 5 shows the composition of gases from an enclosed area in a bituminous mine. A mine fire had once existed in the area and these samples were collected by operators using breathing helmets 9

months after the fire had originated and prior to the reopening of the mine. The oxygen had almost entirely disappeared. The mine is classed as non-gaseous. An accumulation equal to over 5 per cent methane had taken place.

NO. 6 SERIES.

Sample No.	Per cent.					
	CO ₂	O ₂	CO	H ₂	CH ₄	N ₂
1.....	8.07	1.69	1.58	1.37	3.39	83.90
2.....	9.14	1.83	1.32	1.03	3.60	83.08
3.....	2.93	10.34	.56	.13	.82	85.22

Samples No. 1 and 2 in series No. 6 were obtained directly from a fire area, 4 and 7 hours respectively after the mine had been sealed off. The fire occurred just inside the pit mouth of a drift bituminous mine. Samples were obtained by boring holes through the thin roof covering. These analyses with others showed that air was not inleaking to an appreciable extent and the existence of an atmosphere that could not further the progress of the fire. No. 3 analysis of this series represents the atmosphere in the same mine about 1,400 ft. away from the seat of the fire. An entrance was made through another entry in the mine with oxygen helmets, and samples of gas were obtained. The party could not proceed farther because of a heavy pall of smoke. It was impossible to better shut off the air because of various small openings in the outcrop. The oxygen content in sample No. 3 of this series was viewed with some uneasiness, but because of the stagnation of the air and accumulation of black damp it was believed that appreciable diffusion of fresh air into the burning area could not take place. Such proved to be the case.

NO. 7 SERIES.

MINE FIRE GASES.

Sample No.	Date.	Time.	Per cent.			
			CO ₂	O ₂	CO	CH ₄
1.....	Oct. 27	12:00 p. m.	3.5	8.3	1.3	11.5
2.....	Oct. 27	12:00 p. m.	3.8	9.6	.7	13.1
3.....	Oct. 28	9:45 a. m.	3.4	10.9	.6	10.8
4.....	Oct. 28	4:00 p. m.	3.4	11.3	.6	10.3
5.....	Oct. 28	4:30 p. m.	3.0	12.6	.4	9.6
6.....	Oct. 29	11:00 a. m.	3.3	14.1	.6	9.0
7.....	Oct. 29	3:30 p. m.	4.0	13.6	.8	12.0
8.....	Oct. 30	10:30 a. m.	4.8	10.1	1.2	14.1
9.....	Oct. 30	5:00 p. m.	4.0	12.2	1.0	12.2
10.....	Oct. 31	6:30 a. m.	12.2	6.6	.4	6.6

Series No. 7 shows the composition of the atmosphere in an enclosed area of an anthracite mine, while a fire existed therein. The bureau men arrived at the scene of the fire on Oct. 27. Dams were in place and water was being forced behind the dams in an effort to flood the fire area. The dams were placed in stoop pitching chutes, and the water had to roof the chutes at the dams, and from there back up hill in order to reach the seat of the fire. Because of the pitching chutes it was difficult to make the dams hold water. Samples of the atmosphere behind the dams were obtained and analyzed. The first two analyses show the results of the first day's sampling. The two days following, despite efforts to tighten the dams, inleakage of air occurred to such an extent that the fire burst forth with renewed intensity. This happened when the oxygen in Sample No. 6 had risen to

14.1 per cent. The air was inleaking through another dam, and some of the products of combustion were finding exit at the dam where sample No. 6 was collected. The air fanning the fire into a blaze probably contained about 18 per cent of oxygen. After sample No. 6 was taken the fire was again brought under temporary control as shown by the decrease in oxygen. The carbon dioxide and carbon monoxide also rose. Then air again started to inleak and in order to avoid another outburst of fire, a carbon dioxide fire extinguisher was brought into the mine and carbon dioxide was forced behind one of the dams for 5 hours, checking the fire until new and tighter dams could be built. The rise in carbon dioxide due to this cause, is shown by sample No. 10, collected one-half hour after the use of the extinguisher had been discontinued. The new dams held water well, and excluded air so that the fire was rapidly brought under control.

NO. 8 SERIES.

SAMPLES OF NORMAL MINE AIR FROM DIFFERENT SECTIONS OF A MINE WORKING THE PITTSBURGH SEAM.

	Sample No.	Cu. Ft. of Air per min. CO ₂	CH ₄	Cu. Ft. of CH ₄ per min.
	1.....	17,400 .04	.10	.17
	2.....	21,600 .06	.94	203
Return	3.....	63,000 .11	.75	473
Face	4.....	air still .12	1.80	...
Return	5.....	79,800 .15	.19	152
	6.....	21,600 .06	.10	22
	7.....	31,500 .13	.70	220
Face	8.....	air still .11	1.38	...
	9.....	39,200 .15	.75	294
	10.....	8,100 .09	.34	28
	11.....	11,400 .06	.14	16
	12.....	32,400 .09	.94	305
	13.....	23,200 .05	.95	220

Series No. 8 show the carbon dioxide and methane in the normal mine air of different parts of a large mine working the Pittsburgh coal seam at the time the new Pennsylvania mining code was proposed embracing certain features relating to the percentage of methane allowable, one of the mining companies asked the bureau to sample the air in its mines with a view to determining just how much methane was present. Since that time the bureau has trained a chemist for the work, installed a gas analyses apparatus and the company is now having daily analyses made. It can be stated that the bureau will do this much for other mining companies if they desire closer methane determinations than the safety lamp will show. It might be mentioned that the state inspecting department of Alabama, among others, is being given similar aid. The Chief Mine Inspector is installing a laboratory in his office and his men will frequently send in samples.

NO. 9 SERIES.

ATMOSPHERES EXTINGUISH TO FLAME.

Wolf lamp flame, bonnetted:	
CO ₂	3.00%
O ₂	16.50%
Wolf lamp, without bonnet:	
CO ₂	3.00%
O ₂	15.82%
Bunson burner (natural gas):	
CO ₂	3.25%
O ₂	13.90%

Acetylene lamp:	
CO ₂	6.30%
O ₂	11.70%
Candle flame:	
CO ₂	2.95%
O ₂	16.24%

In these experiments, series No. 9, the different flames were placed under a 10 liter bell jar and the atmosphere analyzed after the flames had become extinguished due to the consumption of oxygen. It might be well to call attention to the tenacity to existence of the acetylene flame. In other words it will burn in an atmosphere in which the ordinary flame cannot exist; also that it is bad practice to work in atmospheres deficient in oxygen to the extent these analyses show.

NO. 10 SERIES.

Series No. 10 shows the composition of some gas samples obtained from a mine about 18 hours after an explosion had occurred therein.

No. 1 sample:

CO ₂	1.37%
O ₂	18.14%
CO	.60%
CH ₄	1.23%
H ₂	.28%
N ₂	78.38%

Sample No. 1 of No. 10 series was obtained at the face of an entry by bureau men equipped with oxygen

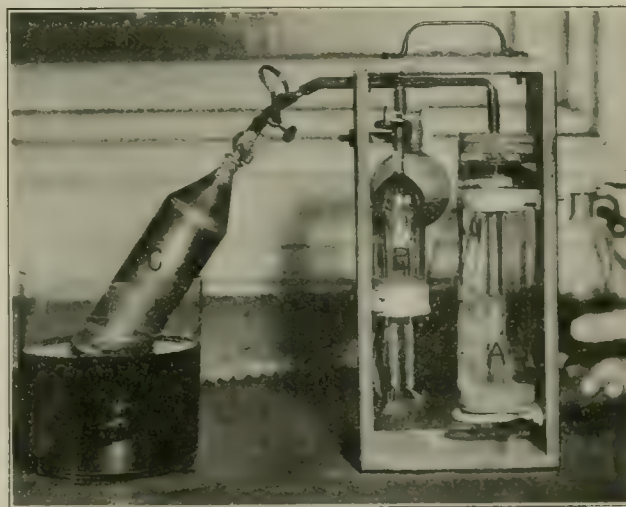


Fig. 1.—Gas Analysis Apparatus.

helmets. The ventilation in this section of the entry had not been restored. The seat of the explosion was supposed to have been close to this place. A canary bird carried by an exploring party, unequipped with helmets, collapsed as it was being carried in this entry about 200 ft. back from the face. The men retreated without suffering any distress. The bird revived quickly when brought back to fresh air. The sample is further interesting in that 1.23 per cent of methane was found to be present. This particular explosion was supposed by some to have been originated by the flash of short circuited electric wires igniting coal dust, but the fact that considerable methane was found at the face, points to the possibility of fire-damp playing some part in the catastrophe.

No. 2 sample:

CO ₂	.32%
O ₂	20.50%
CO	.04%
CH ₄	.19%
H ₂	.00% (below .02%)
N ₂	78.95%

No. 2 sample of No. 10 series was obtained in a section of the mine where ventilation had been partly restored. Even so, .04 per cent of carbon monoxide was still present. Our party and others spent some considerable time in this section without feeling any effects from the whitedamp, although one member stated he did not feel very well. This man had, however, been traversing this and other sections of the mine for 7 or 8 hours, consequently it is very possible that he had been breathing small percentages of carbon monoxide a large part of the time. Eight men lost their lives in this explosion, and at least six of them were overcome by carbon monoxide. Some of the rescue party also experienced very narrow escapes from the after damp. If they had provided themselves with canary birds in the beginning of the exploration work, it is probable that a large part of the distress experienced by them would have been avoided.

Figure 1 shows a simple gas analysis apparatus which has been assembled especially for the use of mine superintendents, foremen and inspectors. Methane can be determined with an accuracy of .1 per cent in less than 10 minutes. It consists of a measuring vessel A for measuring the gas, and a burning vessel B for burning out the methane from a measured volume of mine air. C is the sample pipette. The mine air is drawn into the measuring vessel A from the pipette C, measured and passed into the burning vessel B. The platinum wire therein is electrically heated to a white heat and allowed to remain so for 3 minutes. The current is then broken and the pipette cooled. The mine air is then drawn back into the measuring vessel and the contraction in volume due to the burning of the methane is determined by again measuring the sample. This contraction in volume when divided by 2 and calculated to a percentage basis gives the amount of methane present in the sample. The measuring vessel or burette has a total capacity of 50 cubic centimeters and is divided into the bulb at the top having a capacity of 45 cubic centimeters and the stem which has a capacity of 5 cubic centimeters. The stem is graduated in .05 cubic centimeters or twentieths. Water is used both in the measuring and burning vessels. The apparatus works on no new principal but follows the method adopted by Coquillon, Winkler and others who burn the methane out of a measured volume of mine air.

The Bureau of Mines has assembled other types of gas analysis apparatus more accurate than the one described but which are not simple of operation, and which are meant for the use of chemists.

THE VOLATIL CONSTITUENTS OF LIGNITE.*

By G. B. FRANKFORTER AND ANDREW P. PETERSON.

In the proximate analysis of lignite, the determination of the volatil constituents is unquestionably of great importance, and like the determination of moisture is deserving of special attention. A considerable portion of the volatil combustible matter in lignite, as determined in the proximate analysis of coal, seems to consist of small particles of carbon carried off by the liberated gases and by the moisture. This is evident from the fact that in addition to the flame produced by the burning of the gaseous constituents themselves, particles of solid combustible matter are carried upward by the gases and appear for an instant as glowing sparks before being completely oxidized. These solid particles are especially noticeable if the lignite contains a large amount of moisture or if the determination is made without first thoroughly drying the sample. Even though the crucible lid fits perfectly, these particles are thrown off when the heat is applied as indicated in the ordinary analysis of bituminous coal. The volatil constituents may be varied from 5 to 12 per cent by slowly or rapidly raising the temperature to a red heat. The variation is more noticeable, however, in the undried lignite. It was found that not only the quantity of volatil matter but also the composition of the gas varied, depending upon the heating and whether or not the lignite contained its hygroscopic water.

The first experiments were made with the idea of determining the quantity of volatil matter, both by weight and by volume as compared with good bituminous coal. Accordingly, determinations were made by the ordinary method and by heating in an atmosphere of hydrogen.

The samples examined came from the extreme limits of the Dakota, the Canada and the Alaska coal belts. Samples from these different localities were found to vary considerably in their physical properties, indicating that they must have been formed under different physical conditions. Those from the south are brown, slightly resembling good peat. They contain more moisture than those from farther north. They also seem to slack more readily. One of the characteristic features of the southern lignite is the tendency to break up into more or less laminated forms on losing moisture, while those from farther north, on losing moisture, break up with a slightly conchoidal fracture. The Saskatchewan, Alberta and Alaska lignites are darker than the lignite from the beds of southern North Dakota and slightly resemble ordinary anthracite in both color and fracture.

The regular proximate analyses were made accord-

*From the Journal of the American Chemical Society.

ing to the Report of the Committee on Coal Analyses.¹

As already stated,² the lignites vary widely in the amount of moisture they contain. Some of the samples from the southern belt contain more than 40 per cent of moisture or nearly twice as much as samples from the extreme north. This is due partly to the structure of the coal and partly to the fact that most of the beds in the south are very wet, while most of those in the north are comparatively dry.

In order to make the analyses as nearly comparable as possible, the samples were taken just as they came from the mines and dried in air until they had reached an equilibrium.

Under ordinary circumstances the lignites exposed to the air continued to lose moisture until they reached an equilibrium at from 10 to 12 per cent. At this point the loss of moisture practically stops if the lignite exists in pieces of moderate size. If the samples are pulverized, the moisture drops to 7 or 8 per cent before an equilibrium is reached.

Samples 2 and 3 contain more than the average equilibrium amount of moisture, partly because they seem to be a little more compact, and partly because they were in larger pieces than the others. All of the samples were air-dried in the form in which they came from the mine.

The samples examined were as follows:

1. North Dakota.
2. Saskatchewan, Canada.
3. Alberta, Canada.
4. Klondike in Alaska.
5. Beaver Hill, Alaska.

For convenience, the above numbers have been used to represent the different samples.

The proximate analyses gave the following:

Sample.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Moisture	12.95	15.95	22.50	10.20	11.10
Volatile combustible matter.	36.45	34.40	28.30	36.65	37.20
Fixed carbon	42.77	44.38	45.40	48.40	46.43
Ash	4.83	5.27	3.91	4.75	5.27
Sulfur	0.90	0.82	0.70		

Following the above determinations, ultimate analyses of the first three lignites were made. Calculating to moisture-free samples, the results were as follows:

Sample.	No. 1.	No. 2.	No. 3.
Carbon	62.90	66.42	68.10
Hydrogen	4.30	3.78	4.21
Nitrogen	0.81	1.09	1.12
Sulfur	1.03	0.98	0.90
Oxygen	25.46	21.43	20.67
Ash	5.50	6.30	5.00

Carbon and hydrogen were determined by the regular combustion, nitrogen by the Kjeldahl method and sulfur from the residue of a Parr calorimeter combustion. The ash was calculated from the proximate analysis.

Determinations in an Atmosphere of Hydrogen.—

In order to compare the volatil matter obtained in the above proximate analyses, with result, obtained by heating at the same temperature in an atmosphere of hydrogen, a special apparatus was made, whereby the air could be entirely excluded during the process

of heating. Various forms of apparatus were tried. The one which gave best results (see Fig. 1) consisted of a graphite muffle so arranged that the open end could be securely closed. Through the bottom of the muffle four holes were drilled of such size that platinum crucibles would fit in perfectly. By carefully fitting the crucibles with asbestos paper, they were made practically gas-tight. With this apparatus four analyses could be made at a time. Two small holes were bored through the side of the muffle in order that hydrogen could be passed through during the heating. Known weights of lignite were then placed in the crucibles, the air driven out by hydrogen and the determination made by heating in the regular manner at a red heat. In each case duplicate determinations were made.

The following table shows the difference between the amount of volatil matter as determined in an atmosphere of hydrogen and in air under the same conditions.

Sample.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Volatil matter in hydrogen.	28.51	28.60	28.79	28.65	28.57
Volatil matter in air.....	35.15	36.20	36.50	36.65	37.20

Destructive Distillation.—That the volumes of gas obtained by destructive distillation of the above sam-

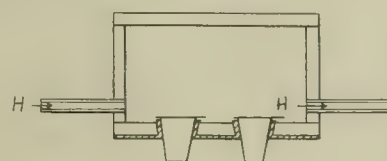


Fig. 1.

ples of lignite might be compared, a series of determinations was made by heating a known quantity of lignite in a platinum distilling flask until all of the volatil material had passed off. The amount of gas was found to vary widely not only in samples of lignite obtained from different localities but also in those obtained from the same locality.

Samples from the far north, including Canada and Alaska, seemed to give more gas than those found further south in the Dakotas.

The following table represents the volumes of gas per gram obtained by heating in a platinum distilling flask at a bright red heat:

Sample.	No. 1. ³	No. 1a. ³	No. 2.	No. 4.
Volume of gas in cc. from dried lignite..	400	376	420	450
Volume of gas in cc. from undried lignite	500	540	601	620

The total quantity of gas was found to vary widely, especially when the long narrow necked platinum distilling flask was used.

On carefully studying the gases, it was found that the variation was due to moisture in the coal, some of which was probably changed into hydrogen and carbon monoxide by the sudden heating of the sample. This was evident from the analysis of the gas. The platinum distilling flask was therefore discarded and

¹Tr. Amer. Chem. Soc. 21, 1116-1145 (1899).

²Ibid., 29, 1488.

³Samples 1 and 1a represent the southern and northern North Dakota lignite. No. 1a came from northern North Dakota and in appearance is a mean between the southern Dakota and Saskatchewan lignites.

a series of determinations made, using a special shaped iron retort so as to avoid the error resulting in the formation of water gas.

The pulverized lignite was placed in the air-tight iron retort and distilled at a temp. of 800-850° until the gas ceased to pass off. The distillates were led into cooled flasks for the purpose of condensing the water and tarry products. Two flasks were used for condensing the moisture and other readily condensable gases. The first one was kept at 25-30°; it condensed practically all of the water and most of the tar. The second was cooled by ice-water; it condensed in addition to a very small amount of water, a white waxy substance which melted at room temperature and which readily oxidized to a dark oily liquid. This white substance was found in all the lignites. It is under investigation at the present time.

The gases were then led into a gasometer but connections were made so that at any time during the distillation, samples of the gas could be drawn off for analysis before they entered the gasometer.

Destructive Distillation of North Dakota Lignite.—North Dakota lignite was subjected to destructive distillation in the apparatus above mentioned. The moisture and the tar were weighed and the gas measured. A number of analyses were made on the same sample.

Three determinations gave the following:

	No. 1.	No. 2.	No. 3.
Fixed carbon and ash.....	52.60	52.40	52.50
Water	27.20 ^a	35.00 ^a	36.30
Tar 1st bottle.....	0.70	0.70	0.70
Tar 2nd bottle.....	0.70	0.30	0.30
Gas at 0° and 760 mm. liters per 100 grams	17.00	12.50	15.50

An average sample from each distillation was then analyzed. Inasmuch as it was not found convenient to remove the air from the apparatus before beginning the experiments, corrections were necessary in order that the true composition of the gas might be determined. These corrections are found under the columns indicated as air-free gas.

Analysis of Gases.

The gases obtained from distillations 1 and 3 were analyzed with the following results:

	—No. 1.—		—No. 3.—	
	Found.	Calculated as air-free.	Found.	Air-free.
CO ₂	36.0	41.0	34.5	38.1
Unsaturated hydrocarbons ..	0.5	0.6	2.0	2.3
O ₂	3.1	1.0	3.6	1.6
CO	11.3	12.8	12.2	13.8
CH ₄			24.5	27.5
H ₂			12.5	13.0
N ₂			10.7	3.7

The quantity of oxygen is unusual. After allowing for the oxygen of the air in the apparatus at the beginning of the process, an excess amounting to over 1 per cent was found in the gas although no signs of leakage in the apparatus could be detected.

The quantity of unsaturated as well as of saturated hydrocarbons is extremely low in all of the lignites. This doubtless accounts for the fact that they are practically smokeless.

Analyses were then made of different samples of gas taken during successive stages of the distillation. The following results were obtained:

Sample taken.	After 500 cc.	After 3 liters.	After 7 liters.	After 8 liters.	After 10 liters.	At end of run.
CO ₂	51.20	45.00	38.00	28.00	26.00	26.00
Unsaturated hydrocarbons	0.10	4.40	3.80	1.20	0.20	0.30
O ₂	5.40	0.20	0.0	0.80	0.20	1.80
CO	5.60	13.60	12.00	15.00	14.40	12.00
CH ₄	0.0	24.40	Not anal.	28.00	26.00	Not anal.
H ₂	0.0	11.30	Not anal.	21.00	20.00	Not anal.
N ₂	37.70	1.10	Not anal.	7.00	4.20	Not anal.

In the early stages of the distillation, carbon dioxide passed off more rapidly than the other gases, as will be seen from a glance at the above table. After about half of the gas had been driven off, the percentage remained practically constant. This, however, was not the case in the other samples examined. The large amount of nitrogen in the first 500 cc. of gas is due to the fact that the air had not been removed from the apparatus.⁵

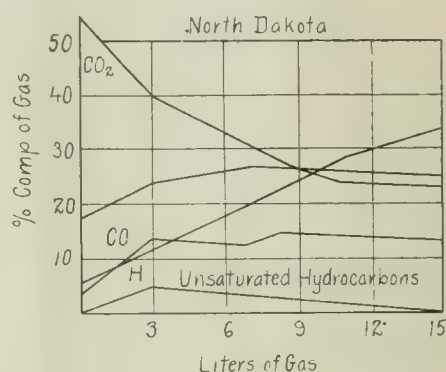


Fig. 2.

The preceding diagram (Fig. 2) will give at a glance the composition of the gas at different stages of the distillation.

Destructive Distillation of Saskatchewan Lignite.

Three samples taken from the mines at Bienfait were subjected to the same process of distillation and at the same temperature as those of North Dakota with the following results:

	No. 1.	No. 2.	No. 3.
Fixed carbon and ash.....	55.50	52.00	52.00
Water	28.00		28.00
Tar 1st bottle.....	0.34		0.40
Tar 2nd bottle.....	0.20		0.20
Gas liters per 100 grams.....	26.00	26.00	26.00

Analyses of average samples of the gas gave the following:

	—No. 1.—		—No. 3.—	
	Found.	Air-free.	Found.	Air-free.
CO ₂	28.00	29.80	27.40	29.30
Unsaturated hydrocarbons ..	0.40	0.40	0.40	0.40
O ₂	1.10	0.0	2.60	1.40
CO	12.40	13.00	15.10	16.30
CH ₄	17.20	18.00		
H ₂	30.00	31.80		
N ₂	10.90	7.00		

^aSome of the water was lost by being sucked back into the retort after distillation.

⁵In order, however, to avoid the error which would have occurred on account of air in the first 500 cc. of gas as indicated in the above tables, analyses were not used in plotting this and other curves until at least one liter of gas had been drawn off. The marks on the curves indicate the points at which samples were taken for analysis.

Analyses were then made of different samples of the gas taken during successive stages of the distillation. The following results were obtained:

Sample taken.	After 5 liters.	After 10 liters.	At end.
CO ₂	55.60	26.00	16.20
Unsaturated hydrocarbons	1.20	1.00	0.0
O ₂	0.80	0.0	0.40
CO	13.00	10.00	17.00
CH ₄	17.20	20.60	14.10
H ₂	12.20	41.30	41.80
N ₂	0.0	1.10	10.50

This gas differed considerably from the North Dakota sample in the total amount of carbon dioxide and in the relative amounts of H and CH₄ evolved, as is graphically shown in the following diagram (Fig. 3).

Destructive Distillation of Alberta Lignite.

Three samples were taken from the mines at Edmonton and distilled exactly as in the previous samples, with the following results:

	No. 1.	No. 2.	No. 3.
Fixed carbon and ash.....	49.90	49.50	48.80
Water	32.10	33.90	32.10
Tar 1st flask.....	1.70	1.50	1.50
Tar 2nd flask.....	0.20	0.20	0.70
Gas liters in 100 grams.....	13.00	18.00	23.00

Analyses of three average samples of the gas gave the following:

	No. 1.		No. 2.		No. 3.	
	Found.	Air-free.	Found.	Air-free.	Found.	Air-free.
CO ₂	14.60	16.80	15.60	16.80	18.00	18.90
Unsaturated hydrocarbons..	0.80	0.90	0.10	0.20	0.80	0.90
O	6.00	4.50	2.30	0.40	0.90	0.0
CO	8.90	10.40	14.20	15.40	14.10	14.80
CH ₄	21.50	24.50	20.30	22.00	24.80	26.10
H ₂	31.30	36.00	32.40	37.70	33.50	35.20
N ₂	16.90	7.90	15.10	7.50	7.90	4.10

Analyses were made of different samples of the gas

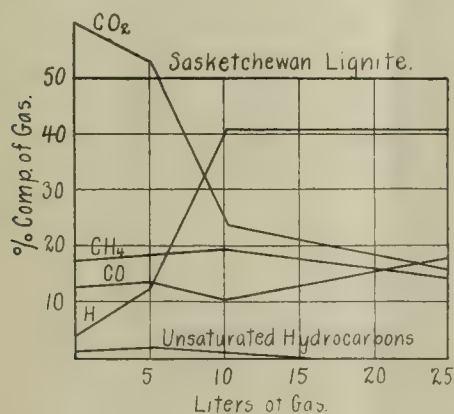


Fig. 3.

taken during successive stages of the distillation, with the following results:

Sample.	After 3 liters.	After 15 liters.	Finish.
CO ₂	21.60	14.80	20.80
Unsaturated hydrocarbons	2.70	0.00	0.00
O ₂	1.90	0.00	0.00
CO	9.40	20.60	16.80
CH ₄	22.20	15.70	9.40
H ₂	24.10	42.60	35.70
N ₂	8.10	6.30	17.30

The accompanying diagram (Fig. 4) will show well the way in which the proportion of gases changes during the distillation.

As the above samples probably represent the extreme range in the composition of the different lignites, the following table will serve as a means of comparing the lignites from the different localities. Averages of three analyses have been taken in most cases.

	N. Dak.	Sask.	Alberta.
Coke	52.50	53.20	49.40
Water	36.30	28.00	32.70
Tar	1.00	0.60	1.90
Gas liters in 100 grams.....	15.00	26.00	18.00

COMPARISON OF GASES (CALCULATED AS AIR-FREE).

	N. Dak. ⁷	Sask. ⁶	Alberta.
CO ₂	38.10	29.80	17.50
Unsaturated hydrocarbons	2.30	0.40	0.70
O ₂	1.60	0.00	1.60
CO	13.80	13.00	13.50
CH ₄	27.50	18.00	24.20
H ₂	13.00	31.80	36.30
N ₂	3.70	7.00	6.50

Comparing the amounts of coke with fixed carbon and ash of the proximate analysis, it will be seen that

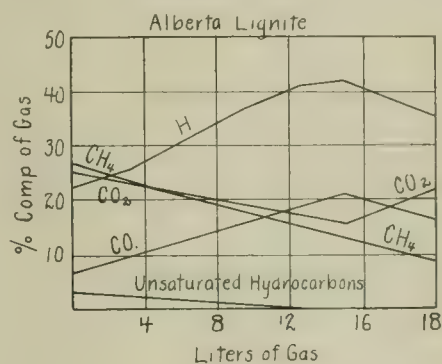


Fig. 4.

there is considerable difference; due, doubtless, to incomplete distillation as the temperature of 830° is evidently not sufficient to drive off all of the volatil matter in some of the samples (see Porter and Ovitz, Bureau of Mines, *Bull. I*). Distillation was apparently complete, however, in the Alberta lignite.

The following table will show the difference between the coke left after the distillation and the fixed carbon obtained by the proximate analysis:

	N. Dakota.	Sask.	Alberta.
Distillation, coke including ash....	52.50	53.20	49.40
Fixed carbon, including ash.....	47.60	49.65	49.30
	4.90	3.55	0.10

The following table shows the relative amounts of hygroscopic water as compared with the total amount found by destructive distillation:

	N. Dakota.	Sask.	Alberta.
Per cent of water obtained by distillation	36.30	28.00	32.70
Per cent of hygroscopic water....	12.95	15.96	22.50
Water produced by distillation....	23.35	12.04	10.20
Per cent of H present (by ultimate anal.)	4.30	3.77	4.21

Calculating the amounts of water found to the dry analysis, the North Dakota lignite would consume 2.98 per cent of the H to form water, the Saskatchewan 1.59 and the Alberta 1.47, leaving respectively, 1.32,

⁶Average sample of distillation No. 1 of the Saskatchewan lignite.

⁷Average sample of distillation No. 3 of North Dakota lignite.

2.18 and 2.80 per cent of H to be evolved either as free hydrogen or in the form of hydrocarbons.

From the above data and from the moisture determinations in samples from different localities it is apparent that the composition of the various lignites depends somewhat upon the locality. The southern samples contain more moisture than those from farther north. The total amount of volatil constituents, however, increases slightly as we go northward. The individual gases seem to vary but not regularly. Carbon monoxide is practically constant and marsh gas changes but little. There is, however, an increase in the amount of hydrogen as we pass northward. On the whole, there is but little difference in the volatil constituents from the different samples, although there is a distinct difference in the general physical appearance.

In a report prepared by Prof. McWilliams, of the Sheffield University, for the meeting of the British Association at Portsmouth, it was stated that up to June, 1910, there were about 118 electric furnaces of all types, of which 70 were in use, 10 were not working, and 38 were being built. There were 77 arc furnaces recorded, of which 29 were credited to Heroult, 17 to Girod, 13 to Stassano, 6 to Keller, and 12 others. (For an account of the furnace at Trollhatten, Sweden, see Daily Consular and Trade Reports for May 6, July 19, and Oct. 14, 1911). Of the induction furnaces there were 14 of the Kjelling type and 15 of the Rochling-Rodenhauser type. The total capacity of all electric furnaces was 350 tons per charge. In June, 1910, there were 29 Heroult furnaces with a capacity of 80 tons in use and furnaces of 50 tons in course of erection, while in June, 1911, there were 43 furnaces with a total capacity of 242 tons.

According to estimates made by the Bureau of Statistics of the U. S. Geological Survey, the imports of silver in 1911 were valued at \$27,450,000 in foreign ore, \$12,850,000 in foreign bullion, \$2,150,000 in United States coin, and \$1,350,000 in foreign coin—a total of \$43,800,000. The exports of silver during the same year were valued at \$135,000 in domestic ore, \$65,000 in foreign ore, \$59,000,000 in domestic bullion, \$4,750,000 in foreign bullion, \$100,000 in United States coin, and \$600,000 in foreign coin—a total of \$64,650,000, or \$20,850,000 in excess of the value of the imports. In 1910 the value of the excess of exports over imports of silver was \$11,482,805; in 1909 it was \$11,404,607, and in 1908 it was \$9,613,541. Previous to 1908 it had not been below \$15,000,000 for several years. The imports of silver in 1911 were, as usual, chiefly in ore and bullion and came mainly from Mexico and Canada. The exports were almost wholly in ore and bullion and went, as usual, chiefly to the United Kingdom and in smaller amounts to Hongkong and France.

FALLACIES IN THE BACTERIAL CONTROL OF A SEWAGE PURIFICATION PLANT.*

Dr. ARTHUR LEDERER and FRANK BACHMANN.

A well conducted sewage purification plant *ought* to be subjected to chemical and bacterial control, just as a well conducted water purification plant *must* be. There is one essential difference, however, in the control of a sewage and a water purification plant, and that is the importance of the control. The effluent of a water purification plant must be free from pathogenic intestinal bacteria as indicated by the various presumptive tests, and also must show a reasonably low count, previous experience serving as a guide. A deeper bacterial study ordinarily is not required nor essential unless special occasion should call for it. The physical appearance of an effluent likewise furnishes a good index of safety. In a water purification plant the bacterial control stands supreme, being far superior to the chemical or physical control. All the sanitary authorities are interested in is whether the water supply is free from harmful organisms, clear, colorless, palatable, reasonably soft and devoid of obnoxious odor and taste. Very little are they concerned about the daily variations in the chemical constituents. The situation is somewhat reversed in a sewage purification plant. The reason for this is simply that the sewage purification plant is not required to absolutely remove all the harmful organisms of the sewage except where the final effluent is to be discharged into a body of water used as a source of a water supply. The object of a sewage purification plant consists in reducing or eliminating the putrescible matter of the crude sewage. Ordinarily the purification of sewage has not to be carried to a stage where the same requirements have to be met, as in the purification of a drinking water, although this is highly desirable unless the effluent is discharged into a large body of water which is used for industrial or agricultural purposes only. Speaking of sewage purification from the standpoint of reducing pollution or preventing a nuisance, but not of making drinking water, the data obtained by chemical analysis are far more important. The routine bacterial work consisting in the enumeration of the total number of bacteria, and probably in the enumeration of the acid formers is of comparatively little importance. The reason for this is simple. Let us assume that a sewage purification plant consists of a grit chamber, primary settling basins, or settling tanks, coarse grain sprinkling filters and secondary settling basins. None of these devices has for its object the destruction of bacteria, although the final effluent of the secondary settling basin shows a very much smaller bacterial content than does the crude sewage. The removal of the bacteria is simply incidental and for the greater part due to the removal of the suspended matter present originally. Certain definite chemical

*From the proceedings of the third meeting of the Illinois Water Supply Association, Urbana, Ill., Feb. 21-22, 1911.

changes are expected in the septic tank and in the sprinkling filter by which the work of these devices can be measured; consequently chemical methods have to be applied to obtain the information. There are also a number of other reasons why routine bacteriological methods cannot supplant routine chemical methods which will be discussed later. The removal of the bacteria in the sprinkling filters is primarily a merely mechanical process, and due to the settling of the floating matter on the surface and in the crevices of the filter material. Secondly, however, these bacteria either die because of lack of proper surroundings or fall a prey to antagonistic bacteria or microscopic and macroscopic animal organisms. Ordinarily as has been said before, the percentage reduction of the bacteria will go hand in hand with the percentage reduction of suspended matter. The only exception being the septic tank where normally an increase of the bacteria takes place which is followed by a decrease as septic action goes on. An attempt to judge the efficiency of a septic tank by a routine bacterial count is therefore ridiculous, even when many samples are taken covering a short period of time. In spite of this one often sees reports on septic tanks from commercial laboratories where much stress is laid upon the bacterial count in the effluents. The bacterial count in the effluent of sedimentation tanks is of more value, although here too the removal of the organic nitrogenous and carbonaceous matter is of the first importance. The greatest drawback in the bacterial control of a sewage purification plant is the fact that it is a physical impossibility to plate enough samples to gain information on what a certain device has done inside a definite period. The collection of samples for the chemical tests is comparatively simple. In the Sewage Testing Station of the Sanitary District of Chicago, the crude sewage is collected hourly covering a period of 24 hours, the total collection being about $\frac{3}{4}$ of a gallon. Hourly samples are likewise collected from the effluent of the purification devices, covering a period of 48 hours. 10 cc. of chloroform are added to the sample bottles which in addition are kept in an ice chest at a temperature of about 10° C., until their contents are analyzed. Such a procedure insures a good average chemical sample of a flow extending over a definite period, but cannot be used, of course, for any bacterial tests. To try to obtain similar reliable information on the number of bacteria in the effluents of the various devices in a large plant, would require a staff of trained men entirely out of proportion to the value of the results obtainable. In a well conducted plant the number of scientific workers is ordinarily limited for the financial reasons to just the number which is essential to obtain the most useful information in the shortest possible time. Since the number of bacterial samples must necessarily be limited one must discriminate carefully in selecting the source of these samples for the routine work. The bacterial count in the various effluents has to be compared with the bacterial count in the crude

sewage. Now the bacterial count will vary during the day just as the chemical constituents. To gain a fair idea of the average bacteria in the crude sewage at least three samples should be taken daily representing the typical morning, evening and night flow. From the other devices equivalent samples should be taken: e. g., if the period of flow in the septic tank is six hours, and the crude sewage sample is taken at 9:00 a. m., the septic sample which should theoretically coincide would have to be collected at 3:00 p. m. If this procedure is followed over a long period of time, the average result will be of some value, otherwise it will not. An occasional bacterial count of the crude sewage or effluent of any purification device means absolutely nothing.

An important factor is the actual collection of the bacterial sample. In a plant where the bacterial count is part of the routine work, constant attention must be given to the sampling. Often a laborer is assigned to collect bacterial samples, particularly when samples are to be taken during the night, or on Sundays. Unless the man is of fair intelligence and very conscientious, the necessary precautions do not mean anything to him, and one after another will be disregarded.

The bacterial samples collected during the night are ordinarily kept in the ice chest until morning, but very often also samples collected during the day are stored for a short period at room or ice box temperature before they can be placed. The question is now how long a sample of sewage can be stored before material changes in the number of bacteria present take place. A considerable number of experiments have been carried on in the laboratory of the Sanitary District to this effect in connection with some other investigations, the period of storage extending over 14 days. In one of the short storage experiments, a crude sewage with a total count of 85,000 bacteria per cubic centimeter increased after two hours storage at room temperature of 22° C. to 105,000, and after 24 hours storage to 350,000. The medium used was in all cases litmus lactose agar, the period of incubation two days, and the temperature of incubation 37° C. On storage in the ice chest at 7° C. an initial count of 125,000 dropped to 55,000 after two hours, to 35,000 after 7 hours, and to 10,000 after 24 hours. The effluent of a sprinkling filter increased at room temperature (22° C.) from a count of 20,500 to 31,500 after two hours, and to 52,000 after 24 hours. At cold storage an initial count of 22,500 dropped to 18,000 after two hours, to 11,000 after seven hours, and to 9,000 after 24 hours. It is evident from these figures which are representative of a large number, that even short storage will influence the number of bacteria. Room temperature will increase, ice box temperature decrease the number, the difference in two hours often amounting to 50 per cent or more. The increase in the bacterial sewage samples at room temperature storage is only temporary however. In one characteristic instance a count of 265,000 in the crude sewage exposed

to room temperature decreased to 105,000 on the third day, to 190,000 on the fifth day, and so gradually until the 14th day, when the count was 4,000. At cold storage a total count decreased from 275,000 to 210,000 on the third day, and so on until it reached 10,000 on the 14th day.

The fact that the bacterial content of a sewage will vary constantly inside of a short period is really the main difficulty in the bacterial control of a sewage purification plant. A large number of experiments has convinced us that it is impossible even to make the bacterial count check from minute to minute. Taking the average of duplicate counts, a sample of a grit chamber sewage may show a count of 70,000 at a certain time, a count of 120,000 after one minute, 170,000 after four minutes, 85,000 after six minutes and so forth. Of course the same must necessarily hold true where samples are taken in intervals of 10 minutes. The following table is an example of bacterial counts in a grit chamber effluent taken every minute for ten minutes, and every ten minutes for 100 minutes.

TABLE I.—FLUCTUATIONS IN THE BACTERIAL COUNT OF A GRIT CHAMBER EFFLUENT. AVERAGE OF DUPLICATE PLATES.

One Minute Tests.			Ten Minute Tests.		
Time from Start in Minutes.	Total Count per c.c.	Time from Start in Minutes.	Total Count per c.c.	Time from Start in Minutes.	Total Count per c.c.
0	70,000	0	220,000	0	300,000
1	120,000	1	200,000	10	330,000
2	130,000	2	190,000	20	200,000
3	170,000	3	270,000	30	250,000
4	230,000	4	390,000	40	220,000
5	85,000	5	550,000	50	220,000
6	120,000	6	530,000	60	280,000
7	100,000	7	470,000	70	100,000
8	80,000	8	subtilis growth	80	220,000
9	110,000	9	350,000	90	140,000

The same variations hold true for the effluent of a septic tank, especially during the warm season when septic action is at its highest, and when sludge is constantly coming to the surface. Effluents of sprinkling filters are likewise subject to wide variations and so are the effluents of coarse grained sprinkling filters. The total count of sprinkling filter effluents is of course much lower.

The following table will give some information as to the variations in the bacterial content of sprinkling filter effluents in one minute interval and ten minute interval experiments.

TABLE II.—FLUCTUATIONS IN THE BACTERIAL COUNT OF A COARSE GRAIN SPRINKLING EFFLUENT. AVERAGE OF DUPLICATE PLATES.

One Minute Tests.			Ten Minute Tests.		
Time from Start in Minutes.	Total Count per c.c.	Time from Start in Minutes.	Total Count per c.c.	Time from Start in Minutes.	Total Count per c.c.
0	16,500	0	2,500	0	7,500
1	13,500	1	3,000	10	7,500
2	18,500	2	3,500	20	7,000
3	13,500	3	3,500	30	6,500
4	13,500	4	6,000	40	8,500
5	9,000	5	4,000	50	10,000
6	9,000	6	2,500	60	17,000
7	12,000	7	2,500	70	7,000
8	12,000	8	2,000	80	8,500
9	12,500	9	2,500	90	11,000

The wide variation in the total count can be easily explained. The micro-organisms are in suspension and are present for the most part in the coarse particles of suspended matter. These coarse particles occur not only in crude sewage, but also in the effluents of coarse grain filters. This likewise explains the fact that duplicate determinations seldom check closely.

It can be easily proven that the suspended matter in a crude sewage sample shows a higher count than does the comparatively clear supernatant liquid. In one case the bottom layer of the crude sewage sample showed a count of 180,000 per cubic centimeter, the top layer a count of 139,000. In another case the bottom layer count was 195,000, the top layer count 161,000. Of course, all samples have to be shaken vigorously 30 to 40 times before plating to get a fair bacterial emulsion, and even then the clumps of organic matter or sludge cannot be broken up thoroughly and the heavier particles will rapidly settle after shaking, thus making an accurate count and accurate check impossible except by chance. This is true not only when sewage samples are plated directly, but also where samples are first transferred into dilution flasks before plating. From experience at the Sewage Purification Plant of the Sanitary District of Chicago, we should say that the difference in the count of duplicates may run anywhere up to 25 per cent on the average in crude sewage and septic tank effluents, and somewhat less in coarse grain filter effluents. Where a dilution of 1:1000 is required, a more accurate result can be obtained by transferring 10 c.c. of the sample into a 90 c.c. dilution flask, and then 1 c.c. of this dilution into a 99 c.c. flask, instead of making a 1:100 dilution first.

One may argue that it is really of little importance whether a crude sewage shows a count of 250,000 or 200,000 on litmus lactose agar since neither of these counts represents the actual bacterial content. This is true where one is concerned with obtaining merely an occasional count in crude sewage, but where it is desired to base the percentage decrease on the number of bacteria originally present in the influent, that is, the crude sewage, it is well to try to obtain accurate comparative figures since absolute figures cannot be obtained.

While the Standard Methods of Water Analysis have done a great deal toward bringing about uniformity in water and sewage analysis, there is still much to be done to bring about closer uniformity in bacteriological work. In many sewage purification works gelatine is used in preference to agar as a medium. Such procedure may approximate closer to the actual number of bacteria present, but will not yield the valuable information which a count of the intestinal acid forming bacteria on litmus lactose agar plate does yield.

Many workers consider an incubation period of 24 hours at 37° C. as sufficient for agar. We have constantly found that a two day incubation period will

bring out not only more colonies, but that the colonies will be much larger and the small and deep colonies much more distinct. The following table will show the difference between the 24 hour and the 48 hour incubation periods in a crude sewage, septic tank effluents and a sprinkling filter effluent.

TABLE III.

	Total count after 24 hrs. incubation.	Total count after 48 hrs. incubation.
Crude sewage.....	100,000	240,000
Septic tank.....	140,000	550,000
Septic tank.....	120,000	820,000
Coarse grain sprinkling filter...	3,000	13,000

Again, of course, it must be admitted that since a comparative count is all that is required in a sewage disposal plant, it does not matter what method of plating or incubation is employed as long as it is done uniformly. A 24-hour count has the advantage of quick information which is at times valuable.

Undoubtedly a routine chemical is superior in value to a routine bacterial analysis, but when it comes to working out special problems, as disinfection or high degree of purification, the bacterial work is superior to the chemical. More is to be expected from bacterial research as time goes on and the different phases of sewage disposal become better understood from a scientific standpoint. The work of sprinkling filters can undoubtedly be traced back to microscopic organisms to a large extent, and so can the self-purification of sewage laden streams. While we know little about these matters at the present stage of the science, it is only fair to assume that bacteriology will not only give us an insight into the actual working of present sewage purification processes, but will also point out the solution of unsolved problems.

Preliminary figures compiled by the director of the Mint, indicate a total domestic production of silver of 57,796,117 fine ounces in 1911, valued at \$31,787,866. The production in 1910 was 57,137,900 fine ounces, of a commercial value of \$30,854,500. The average price of silver in 1911 was 53 cts. per fine ounce, a decrease of 1 cent from that of 1910.

Aside from the important production from the milling of the silver-gold ores of the mines at Tonopah, Nevada, the bulk of silver output is derived from the smelting of crude copper, lead, and mixed ores and concentrates, chiefly from Montana, Utah, Colorado, Idaho, and Arizona and California. According to the Mint figures, the production increased from all these states except Montana, Arizona, and Colorado. In Colorado the production of all metals except zinc decreased. Increased copper production in Alaska added notably to the silver output of that territory. Final figures will probably show increased production of silver from Arizona instead of a decrease, and possibly little change in California.

PURE POTASH.

To meet the numerous inquiries received by the U. S. Geological Survey as to the exact meaning of the terms potash, "pure potash," "potassium," etc., a non-technical explanation has been printed as a part of Bulletin 530-B, on Potash, by W. C. Phalen, just issued by the Survey. The metallic element potassium, represented by the symbol K, is the basis of all potash salts, but the combination of potassium with oxygen, represented by the symbol K_2O , has been generally adopted as the standard for measuring the potash value of the various kinds of potash salts. As a matter of fact, K_2O does not exist commercially, being merely used as a convenient standard. The following table shows the "potash" or K_2O in the several commercial potash salts and minerals:

Name.	Percentage of potassium	Chemical equivalent in terms of "potash" (K_2O).
Element.	Symbol. (K).	
Potassium	K	100
Potassium salts or "potash" salts—		
Potassium chloride ^a (mineral sylvite)	KCl	52
Potassium muriate (same as chloride)		63
Potassium sulphate.....	K_2SO_4	45
Potassium nitrate (saltpeter) ..	KNO_3	39
Potassium hydrate or caustic potash	KOH	70
Potassium carbonate.....	K_2CO_3	57
Potassium cyanide.....	KCN	60
Stassfurt minerals—		
Carnallite	K M g Cl ₃	14
	6H ₂ O.	
Kainite	M g S O ₄	16
	KCl.3H ₂ O	52
Sylvite (potassium chloride) ..	KCl.	63

With these values in mind it is therefore easy to determine the real potash content of any potash-bearing mineral. Thus a fertilizer carrying 60 per cent of sulphate of potash would contain 32.40 per cent of "potash," or K_2O . If pine wood ashes were guaranteed to carry 13 per cent of potassium carbonate, they would as a matter of fact contain only 9 per cent of K_2O . Again, a compound carrying 90 per cent of sulphate of potash would contain but 48.6 per cent of K_2O , while another compound carrying 80 per cent of chloride of potash (or muriate of potash) would be equivalent to 50.4 per cent of K_2O .

Potassium carbonate was for a long time the best-known potash salt, being the residue from boiling lye from wood ashes in iron pots, whence the name potash.

According to preliminary figures compiled by the director of the Mint the gold production in Colorado was \$19,153,860 in 1911, against \$20,526,500 in 1910; and the silver output was 7,530,940 fine ounces, valued at \$4,142,017, against 8,523,000 ounces, valued at \$4,602,400, in 1910.

^aPotassium chloride is in the trade known by the chemically obsolete term, "muriate of potash."

GAS CALORIMETRY.*

The report of the Calorimetry Committee for 1911 must follow somewhat the lines of the report presented last year; namely, one of progress. While considerable experimental work has been done, the results are not conclusive enough to permit of publishing completely the data obtained during these tests. We are including, however, some few recommendations that we think will be of value.

The experimental work during the last year has included the time of two engineers covering a period of nearly three months. This work was done at the University of Wisconsin, Madison, Wis., by Mr. J. N. Lawrence, under the supervision of Mr. O. L. Kowalke, and at the Philadelphia Laboratories of the United Gas Improvement Company, by Mr. Maurice S. White, under the supervision of Mr. J. B. Klumpp.

The laboratory work consisted of testing for general efficiency a Parr gas calorimeter, submitted and loaned by the Standard Calorimeter Company, East Moline, Ill.; a Doherty gas calorimeter, submitted and loaned by the Improved Equipment Company, of New York; an improved Junkers calorimeter, purchased from Junkers & Company, Dessau, Germany; and a calorimeter of the Junkers type, purchased from the American Meter Company, New York.

The results obtained with some of these new type instruments, as reported by the two laboratories, do not exactly coincide, and, while the errors obtained are not excessive, the discrepancies are great enough to warrant a continuance of the investigation as to the accuracy of these instruments in reading correctly the calorific value of the gas. However, the work has progressed sufficiently to warrant our making certain general statements as to some of the relative merits of these calorimeters.

That of the American Meter Company gives results sufficiently correct for general use and adoption by the members. This instrument embodies the general design of the original Junkers' instrument, and seems to have included the elements that have given that calorimeter its general high efficiency. It is modified, however, according to the recommendations submitted in the Committees' report for the years 1908 and 1909, and is provided with accessories that read directly the heating value, making all measurements in English units.

The results of the two investigations on the Doherty calorimeter have not exactly coincided, and, while they have indicated that this instrument gives exceedingly close readings to those obtained on the Junkers, we feel that our work should be carried somewhat further before any definite statement is made.

In the report of the Committee (1908) it was recommended that the thermometers reading the tem-

perature of the inlet and outlet water be placed on the same level. Such a type of instrument was purchased from the Junkers' Company, Dessau, Germany, and the tests on this one calorimeter do not accord with their original type of calorimeter, but were found to be 2 or 3 per cent lower. This error, it is believed, is caused by a modification of its interior and exterior construction and not by the change of position of the thermometers.

The Parr gas calorimeter represents an entirely different method of obtaining the heating value of the gas. It is a dual calorimeter, and with it a comparison is made between the heating value of the gas to be measured and a gas of a supposedly known heating value. The design and operation of this instrument introduce elements that are not conclusively substantiated, and the results of the observations on this instrument by the two laboratories have been somewhat at variance. It is, therefore, considered advisable to continue this work to determine, if possible, the cause of these discrepancies. Therefore, additional tests will be made, and will be compared with those now being undertaken by the Bureau of Standards.

Further, the work of the Committee has been devoted towards checking the variations introduced by changing atmospheric conditions, and also towards determining the most advisable rate of gas consumption in some of the calorimeters under investigation. The results did not vary perceptibly from the statements submitted to the Institute in previous reports.

During the past year your Committee has been in touch with the Bureau of Standards, at Washington, which has been conducting a very complete examination into the subject of gas calorimetry. The Bureau has obtained instruments of many makes, and the investigation is proceeding along lines, the results of which, when made public, will be invaluable to the gas industry. This work has been undertaken by the Bureau at the request of gas interests, particularly at the request of the American Gas Institute.

After a conference with Dr. E. B. Rosa, Acting Director of the Bureau, and a visit to the laboratories, we are led to believe that it will be wise for us to submit a progress report until we learn about the result of this work, which is being made along lines parallel to the work done by your Committee in the past.

We wish to submit to the Institute a letter, just received from Dr. Rosa, in which he states that, so far as their work has gone, their conclusions agree in the main with those reported by your Committee.

The Bureau of Standards, in its investigation up to this time, has called to our attention some features that should tend to increase the efficiency of operation, and which we thought wise to bring to your consideration. One of these matters is the application of a set of baffle-plates to the Bunsen burner in the Junkers type of calorimeter, that will tend to prevent loss of heat by reducing the downward radiation from the gas

*From the report of Committee at recent annual meeting of the American Gas Institute.

flame. These plates (three in number) are constructed of light metal with several holes to allow admittance of air; they are slipped over the stem of the Bunsen burner and placed about an inch apart, the upper one being about an inch below the top of the burner.

The lower plate is flat and extends to within $\frac{1}{8}$ to $\frac{1}{4}$ in. of the walls of the combustion chamber. The two upper plates are conical in form, and are placed with the apex down, the middle one having a somewhat larger diameter than the upper one, but less than the lower, or horizontal, plate. These baffles should each have four or five holes about $\frac{1}{2}$ in. in diameter, which, with the space between the plates and the combustion chamber, will permit of the passage of sufficient air for perfect combustion of the gas.

Such a scheme has increased the readings of some instruments investigated by the Bureau somewhat higher than 1 per cent, and should be generally adopted.

For the best and most accurate work, and especially where the readings of the calorific power of the gas are made to comply with some regulatory order, it is always advisable to select the best grade of thermometers. These should be calibrated and the correction, if any, applied to the temperature reading.

One manufacturer of thermometers has brought up the subject of the stem correction, that it is necessary to apply if the thermometer is calibrated when completely immersed, which is the general practice, and that adopted by the Bureau of Standards. The stem correction is applied when the stem of the thermometer is exposed and at a different temperature from the immersed bulb. Such a correction is not usually necessary on the thermometer indicating the temperature of the inlet water, as this water, when operating under the directions formerly prescribed, is at the temperature of the room. However, the thermometer indicating the temperature of the outlet water has a stem temperature of probably 15° below the bulb temperature, and, therefore, a correction should be made for the difference in expansion between the mercury and the glass.

The usual correction for a thermometer indicates the error in the reading when the thermometer is completely submerged, as compared with a standard thermometer, under the same conditions, and this correction can be readily applied for any point in the thermometer scale from the correction curve accompanying the thermometer. The correction for the emergent stem is somewhat more complicated, and can be explained in no better way than to refer to "Form 44," issued by the Bureau of Standards. A copy of that form is as follows:

*Correction for Emergent Stem (Thermometer).—*In general, all corrections are determined for total immersion, *i. e.*, for the condition where both bulb and stem of the thermometer are at the same temperature. If, however, the stem is emergent into space either

hotter or colder than the temperature of the bulb, a stem correction must be applied to the observed reading in addition to the correction given in the accompanying table.

This so-called stem correction is very large, if the number of degrees emergent and the difference of temperature between the bath and the space above it are large. It may amount to more than 20° C. for measurements made with a mercury thermometer at 400° C. (750° F.)

For the glass of which this thermometer is made the stem correction may be computed from the following formula:

$$\text{Stem correction} = 0.000088 \times n (T - t.)$$

n = number of degrees emergent from the bath.

T = temperature of bath.

t = mean temperature of the emergent stem.

The mean temperature, t , may be approximately measured by means of a small auxiliary thermometer suspended near the emergent stem, or by surrounding the latter with a small water jacket and taking the temperature of the water with the auxiliary thermometer, or, more accurately, in the way suggested by Guillaume, by exposing an exactly similar stem and capillary mercury thread beside the emergent stem, and thus measuring its mean temperature. This is also conveniently carried out with the "thread thermometer" (Faden-thermometer) of Mahlke, in which the expansion of the mercury in the capillary tube (bulb) is measured on a still finer capillary stem.

Example.—Suppose that the observed temperature was 85 and the thermometer was immersed to the 32 mark on the scale, so that 53 of the mercury column projected out into the air, and the mean temperature of the emergent column was found to be 70 ; then, Stem correction = $0.000088 \times 53 (85 - 70) = 0.07$.

As the stem was at a lower temperature than the bulb, the thermometer read too low, so that this correction must be added to the observed reading to find the reading corresponding to total immersion: *i. e.*, $85.00 \div 0.07 = 85.07$. From the accompanying table of corrections it is seen that a further correction of 0.12 must be applied to the reading of the thermometer at this temperature, so that the correct temperature is $85.07 + 0.12 = 85.19$.

In connection with the work this year we have commenced an investigation into the merits and defects of the small wet gas meter, which is in general use with most calorimeters, and also with most photometers. Our plan is to determine, if possible: First, the error caused when the gas passing through the meter differs in temperature from the water in the meter; second, the effect caused by gases of different degrees of saturation; third, the degree of accuracy with which the meter may be commercially relied upon to register.

There have been several calorimeters called to our attention by members as well as manufacturers, which present exceedingly interesting features, but which we have not been able to look into. We refer more par-

ticularly to instruments of the recording type, but we would advise our members to adopt them with extreme caution. Instruments of this type, while giving comparative results, do not, as a rule, give correctly the actual heating value of the gas, as determined by their indications, and such instruments should not be used for obtaining readings for inspection of regulatory purposes.

On account of the unfinished condition of the work that has been in progress this year, we suggest that the Committee be continued and be allowed to carry on the investigation during the coming year. If this is done it will also afford the Institute an opportunity to keep in touch with the work now under way at the Bureau of Standards, and also other investigations undertaken by several university authorities.

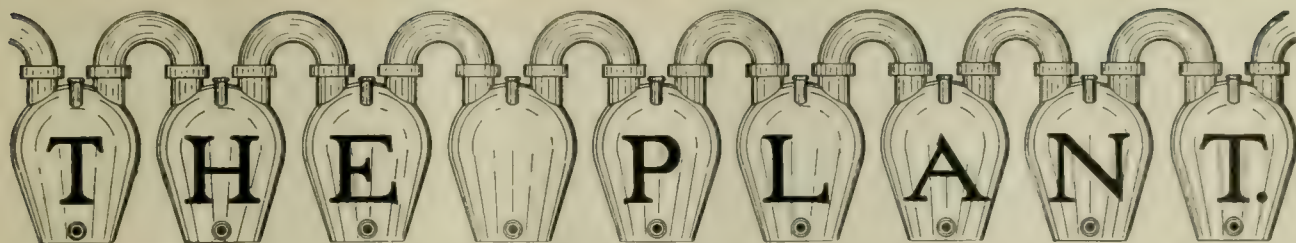
According to preliminary figures of the Director of the Mint Idaho produced in 1911 gold valued at \$1,169,261 and 7,507,802 fine ounces of silver, valued at \$4,129,291, against \$1,035,900 in gold and 7,027,000 ounces of silver, valued at \$3,794,600, in 1910.

The U. S. Consul at Tahiti, Society Islands, reports that the French company, now exploiting the phosphate deposits at Makatea, an island of the Society Group, about 120 miles northeast of Tahiti, has over 600 persons at work on the island. It is estimated that the island contains 10,000,000 tons of high-grade phosphate, averaging 82 per cent, with many million tons more of inferior quality. The force now at work in Makatea can furnish and load about 100 tons of phosphate a day, but this can not be regularly kept up at present, owing to the almost constant rains during the summer months and to the fact that all the drying is dependent upon the sun and the crushing upon human force. An English engineer from Ocean Island has been at Makatea installing an electric plant of 240 H. P. for lighting the island, for propelling the cars carrying phosphate, and also to run the crushing and drying plant now under construction. When this undertaking is completed, about February, 1912, 15 tons can easily be turned out each working hour. The present intention of the company is only to extract, dry, and crush the phosphate at Makatea. In 1910 there were 10,000 tons of phosphate exported; this year the figures will reach 30,000 tons; and it is hoped that the 1912 shipments will reach 100,000 tons, which is the amount estimated as necessary to export yearly for the investment to be a paying one. The shipments during 1911 to the United States included 1,160 tons to California and 1,339 tons to Honolulu (one more shipment of about 1,400 tons will be made to Honolulu before the new year), all of which has been declared at \$9.65 a long ton. There is 15 cents export duty collected by the Government here on each ton shipped.

ESTIMATED PRODUCTION OF IRON ORE IN 1911.

Preliminary estimates of iron ore sold in 1911 were sent to the Geological Survey by 26 of the largest iron-mining companies in the United States at the close of the year. The combined output of these companies represents more than 80 per cent of the total production of the United States. From these returns it is estimated by E. F. Burchard, of the Survey, that the total quantity of iron ore marketed in the United States in 1911, not including stocks left at the mines, was between 43,000,000 and 46,000,000 long tons. This quantity represents a decrease of 22 to 24 per cent of the sales for 1910, which aggregated 56,889,734 long tons. The output for 1910 was the largest quantity of iron ore ever marketed in a single year in the United States, and according to the present estimate the quantity produced in the year 1911 will take fifth place, being exceeded by that of 1910, 1907, 1909, and 1906 in the order named. It is estimated that of the ore produced in 1911 between 39,250,000 and 42,000,000 long tons was red hematite, the remainder consisting of brown hematite, magnetite, and iron carbonate ores. According to the returns received the Lake Superior district, in Minnesota, Michigan, and Wisconsin, apparently produced between 33,000,000 and 35,000,000 long tons of red and specular hematite which represents a decrease of 23 to 28 per cent compared with the production of 1910—46,328,743 long tons. In the Birmingham district, Alabama, the second largest iron-mining center, the production of iron ore apparently decreased 18 to 20 per cent from that of 1910, the estimated production for 1911 being between 3,050,000 and 3,125,000 long tons, compared with 3,802,115 long tons in the preceding year. The ore mined in the Birmingham district consists of red and brown hematite in the proportion of about 4 to 1. The production of iron ore in Tennessee and Virginia apparently decreased only about 16 per cent, according to reports from the principal producers in those States. As the production of pig iron for 1911 may exceed 23,500,000 tons, a larger production of iron ore might appear to be required than has been estimated above, but it must be considered that at the close of 1910 there was 9,408,235 long tons of iron ore in stock at the mines in the United States, and that of this total 8,471,108 long tons was at the mines in the Lake Superior district. Just how heavily this surplus stock of ore was drawn upon in 1911 it is impossible to state at present but owing to the increased activity in the manufacture of pig iron toward the close of 1911, it is probable that the 1910 surplus was in part cleaned up and that at the end of 1911 only a relatively small quantity of iron ore remained at the mines.

The gold production in California in 1911 was valued at \$20,310,987, as against \$20,441,400 in 1910.



THE GAS POWER FIELD FOR 1911.*

By ROBERT H. FERNALD.

The past year of the Gas Power Section has been one of continued prosperity. The progressive policies pursued by the executive committee and the various technical committees during the four short years since the birth of the section, have placed it definitely on a basis that assures its future. The reason for its being and the firm belief in a large future for the organization are readily understood by reviewing briefly the steady, healthy development of gas power during the past year—a year that places gas power for large units well beyond the uncertainties of the purely experimental period.

Large Gas Engine Units.—The development of large gas engine units has gone steadily forward for the past decade. The first engine of this class was that exhibited by the John Cockerel Co. at the Paris Exposition in 1900. This was an engine of 600 H. P. rating. At the present time 1,500 H. P. in each cylinder of the four stroke cycle type and 2,000 H. P. in each cylinder of the two stroke cycle engine, are reported as one of the exhibits at the recent exposition at Brussels. This means units of 8,000 H. P. of the twin tandem double-acting type. The present status of the large blast furnace gas power plants has been ably and thoroughly presented at recent meetings of this section, and the papers and discussions form a valuable portion of the proceedings of the society.

It is understood that at least one company is prepared to install gas engine plants of large power capacity at a cost not exceeding and in some instances less than that of the corresponding steam turbine installations.

Application of the Diesel Engine.—Although the steam turbine has superseded the reciprocating steam engine for electrical development in central station work, and will probably hold the field for some time to come, it is interesting to note that the Diesel engine, owing to its great success in small station service, is looked upon seriously as a possible rival to the steam turbine within a short time. In a paper recently presented before the Municipal Electrical Association at Brighton, England, the relative cost of a 10,000 Kw. installation for steam turbines, gas producers and engines, and Diesel engines, was discussed at length. The author's proposition was to use seven sets each of

1,450 Kw. capacity. Their figures of operating expense, etc., are decidedly in favor of the Diesel engine installation.

Attention was also called to the very economical use of these engines as a substitute for substation converting machinery. Such stations are already putting in their appearance in London.

In this connection it is interesting to note the development in point of size of the Diesel engine. Engines of a few hundred horsepower have become common in European practice. In Swiss electric stations, Diesel engine units of 2,000 H. P. are now in use, and one writer on the subject states that the development of the large sized Diesel engine has been so successful that it will not be long before 1,000 H. P. developed in one cylinder will be thought nothing extraordinary. One company of world-wide reputation is at present considering more than 2,000 H. P. in the single cylinder of Diesel engines. It is stated that engines of this type with four cylinders developing 1,000 H. P. each can be made as light as the corresponding triple expansion engine.

The weight of such engines compares favorably with that of the corresponding turbines and boilers. It is understood that a 1,000 H. P. installation of this type weighed only 187 lbs. per horsepower as compared with 180 lbs. for a steam turbine and boiler installation.

The crude oil engine is now definitely under consideration for all types of marine craft. For small vessels the advantage is the safety afforded by the use of crude oil as compared with the lighter oils. The crude oil engine is being used by many of the principal navies of the world for sub-marine boats and designs are already under way for comparatively large engines for torpedo boats and other similar craft.

A few months since, the *Vulcanus*, a vessel of 1900 tons displacement, 196 feet long, equipped with six cylinder, four cycle single-acting reversible Diesel engines, was put in regular service between Holland and Borneo. This engine is about 500 B. H. P. capacity at 180 r. p. m. The fuel is a crude oil from Borneo and the quoted guarantees are 0.42 lb. per B. H. P. hour at full speed; 0.44 lb. at three-quarters speed, and 0.5 lb. at half speed. In a recent trip the *Vulcanus* covered 3,312 miles in 19 days and 3 hours. The average speeds varied from 6.86 knots to 7.80. It is understood that the average consumption for this ship amounts to one ton of fuel oil per 100 knots.

The technical journals of recent date record many

*Report presented at the Pittsburg meeting of the American Society of Mechanical Engineers.

such installations. Among these Russia is credited with at least four freight vessels of 1,000 H. P. and two 14-knot gun boats of the same horsepower rating.

This month two vessels nearly 400 ft. long of 7,000 tons capacity each fitted with Diesel engines of 2,500 H. P. rating, and with two auxiliary Diesel engines aggregating 500 H. P., will be tried out in European waters.

A recent announcement is to the effect that the Hamburg-American Company proposes to build an ocean liner using Diesel oil engines for motive power.

An interesting comparison will shortly be placed before the public by the British admiralty, as it is proposed to try out side by side in a twin screw a steam engine and a Diesel engine of 6,000 H. P. rating.

Another destroyer recently ordered by the British Admiralty, according to current reports, will have on each shaft a steam turbine and a Diesel engine. The plan is to operate, the turbines when high speeds are required but under cruising conditions, when the speeds are low, owing to the poor economy of the steam turbines, the Diesel engines will be used. The combined economy due to this arrangement will be exceedingly interesting.

One of the interesting features of these engines is the fact that there seems to be a marked tendency toward the two cycle for marine work.

With the introduction of these engines the discomfords of the stoke hole will be greatly reduced and the amount of labor required will be less than under present marine conditions and the character of labor much improved.

Although not probable that steam installations are to be rapidly displaced in the larger ocean-going craft, yet the crude oil engine seems to be especially adapted for such service as that previously indicated. The fuel needed approximates a third of that needed for the steam engine, thus greatly increasing the radius of action if the same weight of fuel be carried. Boilers can be done away with and their space utilized for carrying cargo.

It is reported for a freight vessel of 2,700 tons that a saving of over \$19.00 per day was made by using oil at approximately \$11.00 per ton instead of coal at about \$3.00 per ton.

Tar as a Fuel for Diesel Engines.—Tar oil has become more or less common as a fuel for Diesel engines of 600 or 800 H. P. rating and it is understood that it is used in at least one engine of 4,000 H. P. rating. Recent experiments indicate that both thin gas retort tar and thick coke oven tar can be used in a similar manner by injecting into the cylinder a small percentage of light oil to assist in igniting the tar. It is claimed that a wide range of tars can be used in this manner without producing smoke or appreciable residue. In tests at the Korting works about two per cent of the ignition oil was used at full load and about 13 per cent at half load. Reports indicate that an or-

der has been placed for a 600 H. P. Diesel engine to operate on raw tar.

Internal-Combustion Engine Locomotives.—Locomotives using internal-combustion engines and operating on the standard gage track have recently been put into service. The range of fuel for these engines covers gasoline, benzol, alcohol, and petroleum.

The Prussian State Railways are reported to be operating a 1,000 H. P. locomotive using a Diesel engine as motive power.

Gas Turbine.—Results are soon to be expected from the more recent investigations and tests relating to gas turbines. It is believed that some of the types are based on correct principles and that after a rotary air compressor of satisfactory design has been secured rapid progress in the development of this prime mover may be expected.

Reliability of Internal Combustion Engines.—Not only do the renewed and increased orders for internal-combustion engines by the great manufacturing corporations indicate a feeling of assured reliability, but the subsidizing by European war departments of petrol motor Larries indicates a feeling of reliability in the internal-combustion principle that is beyond dispute. These vehicles will be held subject to purchase in case of need by the war department. An important stipulation is "The engines must be of the internal-combustion type using petrol, and by preference having four cylinders."

The Humphrey Pump.—This internal combustion pump has been before the gas power public for two or three years past. Many similar internal combustion pumps are clamoring for admission to the field. The comptroller in discussing the validity of the Humphrey patents states: "The Humphrey pumps show an important advance in the art. Although many applications have been filled for patents since 1858, none has embodied the principles of the Humphrey pump."

The 1,000 H. P. pump occupies about the same space as the tandem double-acting gas engine of the same power.

Mr. Humphrey says, "With the compression pressure of 11 atmosphere absolute the theoretical thermal efficiency of the cycle is 52.5 per cent, whereas that of the Otto cycle is only 40 per cent when all corrections for varying specific heats are allowed for. With very moderate compression, under 50 lbs., an actual thermal efficiency of 23 per cent has been obtained on a four-cycle Humphrey pump. This corresponds to .95 lbs. of anthracite per hydraulic horsepower hour, and was obtained on a list of only 35 ft."

Utilization of the Waste Heat of the Gas Engine.—Various methods of utilizing the waste heat of the gas engine exhaust have been attempted from time to time and the demand for such devices for heating buildings has been considerable. Several schemes for accomplishing this result are now commercially in

use, but according to recent opinions the most efficient method of utilizing the exhaust is through a combination of gas and steam engines.

Present practice indicates that about 3 lbs. of steam are generated per B. H. P. hour by means of exhaust boilers.

According to Mr. Chorlton the use of exhaust boilers with efficient steam engines and specially designed gas engines of the two-cycle type will effect marked thermal economics and reduced initial cost of the installation per horsepower.

One of the technical journals states that Mr. Chorlton shows by numerical examples the possibilities of such an engine, first examining the case of the addition of a steam end to a normal economical gas engine. He assumes a standard engine to use 9,500 B. t. u. per B. H. P. hour. As the engine is ordinarily arranged with jacket feed to the boilers we may take 40 per cent of this amount to be recoverable. From this at 80 per cent efficiency of conversion at 100 lbs. pressure, we would recover about $2\frac{1}{2}$ lbs. of steam per B. H. P. hour. This amount in an ordinary simple steam engine would not give more than 10 to 12 per cent of the main engine power, a return which hardly justifies the first cost of the steam cylinder. Consequently no development has taken place in this direction.

When, however, we are dealing with a special combined compound engine, each part of which is made in the most suitable way for the purpose required, we get a very different result. In order to reduce the cost of the gas engine part the compression would be lowered and with the ignition retarded a much lower maximum pressure and temperature would result; the total heat units used would go up to, say 12,000 B. t. u., but more would be rejected to the exhaust, and with a special arrangement of boiler, economizer pipes, superheaters in exhaust, etc., 50 per cent waste heat should be recoverable. There should be obtained from this 4 pounds of steam per B. H. P. hour.

The steam cylinder used would be similar in type to that of the two-cycle engine—that is, with no exhaust valves. The unidirectional-flow engine of this type has been largely reintroduced in Germany with very economical results. The jacketing of the ends could be done by exhaust gas. For small engines of this type it is safe to assume a steam consumption of 12 lbs. per B. H. P. hour; a consumption of 10 lbs. has been obtained in actual practice. Hence, the power obtained from the steam cylinder would be one-third of that of the gas cylinder, and the consumption for total effective power would be reduced to 9,000 B. t. u. per hour, less than that for the economical gas engine alone.

Surface Combination.—By what he terms “surface combustion,” Professor Bone reports for gas fired boilers evaporations of 21.6 lbs. per square foot of heating surface and an efficiency of heat transmission

of 94 per cent. The heat balance of a test reported by him shows:

Gas burned per hour (at 32 degs F. and 14.7 lbs.), 997 cu. ft.
 Net calorific value of gas, 562 B. t. u.
 Total heat supply to boiler per hour, 559,800 B. t. u.
 Temperature of feed water, 42 degs. F.
 Pressure of steam, 100 lbs.
 Water evaporated per hour, 450.3 lbs.
 Water evaporated from and at 212 degs. F., 550 lbs.
 Heat transmitted to water, $450.3 \times 1,172 + 527,800$ B. t. u.
 Heat ratio, $527,800 + 559,800$, 943.

In the reports of the surprising results of these investigations, attention is called to the fact that the combustion was perfect as was shown by analysis. An efficiency of 94 per cent was obtained. Deducting 4 per cent for the power required for supplying air pressure still leaves 90 per cent.

Professor Bone says, “The new boilers could be set up in brick work and require no elaborate flume or chimneys. They are liable to no strains as they are short. With some sacrifice of efficiency, the evaporation could be raised to 30 lbs. per sq. ft. The steam was raised quickly (steam at 100 lbs. pressure obtained in 20 min. from cold start) and tubes could be grouped and cut out separately so as to vary the fuel consumption to suit the fluctuations of load.”

Sixty-five per cent of the steam was generated in the first foot of the tubes; 25 per cent in the second foot, 10 per cent in third.

Producer Gas from Low Grade Fuels.—Progress is steadily being made in the utilization of lignite, peat, and high ash coals in producer gas work. The investigations of the Canadian Government show that peat can be prepared for fuel purposes at a cost averaging from 30 per cent to 40 per cent of that of an equivalent B. t. u. value in anthracite in Canada.

As the foundation of a method that may result in extensive use of high ash fuels without prohibitive cost of operation, attention is directed to the present producer-gas investigation of the United States Bureau of Mines, resulting in the successful fusing of the ash and the use of water-cooled producer linings.

In line with this specific conservation of fuel resources it is interesting to note that one estimate states that the U. S. Steel Corporation alone, through its installations of blast furnace gas engines, displaces, or saves, a consumption of approximately a million tons of coal per annum as against the old fashioned methods.

Small Producers for Bituminous Coal.—Reports are persistently before us indicating the successful development of gas producers of small power to operate on bituminous coal, coke breeze, anthracite screenings, “front and cinders,” etc.

Such plants are in great demand, but it is doubtful whether the development and application have been as great as the advertising these plants receive. It is interesting to record, however, that a company, manufacturing anthracite gas producers and gas engines, that expressed in 1904 its firm conviction that the Government tests with bituminous coal in producers

would fail utterly, recently put itself on record as recommending the use of its own engines with small bituminous producers manufactured by another company.

Crude Oil Gas Producers.—The development of the crude oil gas producer for which there is great demand, in oil regions remote from the coal field, has been exceedingly slow but it is believed that very definite progress has recently been made along this line. The most recent notes on this subject relate to the Grine Oil Producer. In this type steam spray is used for atomizing the oil which is introduced into the upper part of the generator where partial combustion takes place. The down-draft principle is then applied and the hydrocarbon broken up and the tar fixed by passing through a bed of incandescent coke. Mr. Grine reports that a power plant using one of these producers has been in operation a year in California. With crude oil as a fuel costing 95 cents per barrel, or 2.3 cts. per gallon, the plant is reported to develop the same amount of power per gallon of crude as is ordinarily developed by the standard internal combustion engine operating on distillate at 7 cts. per gallon. Including the cost of fuel, labor, supplies, interest, depreciation and taxes, Mr. Grine states the cost per B. H. P. hour to be 0.76 cts. for a plant of 100 H. P. rating.

Future Investigations.—The opportunity for investigation in the gas power field is at present unlimited as is evidenced by the fact that nearly a hundred important gas power problems are at present on file at the U. S. Bureau of Mines under the head of "Proposed Investigations."

Conclusion.—It is gratifying to note that each year eliminates many of the absurd prophecies regarding the elimination of practically all prime movers save the internal combustion engine and that the past year may be regarded as one of steady, conservative progress and development in the field that is of such keen interest to so large a percentage of the total membership of the American Society of Mechanical Engineers.

An English company is being formed in Cornwall, England, to build and operate a sugar-beet factory. The business will probably be inaugurated within the next six months.

The silver-mining industry as such is of relatively small importance in the United States, according to H. D. McCaskey, of the United States Geological Survey, but the domestic silver production, depending largely on the output of gold, silver-gold, copper, and lead ores, is equal in value to that of lead or zinc. Owing largely to the prosperity of the gold, copper, and lead mining industries there was an output of silver in 1911 estimated at 57,796,117 fine ounces, which is 2,182,997 ounces more than the average annual output of 55,613,120 ounces of the preceding decade and 658,217 ounces more than the output of 1910.

CLAY PRODUCTS OUTPUT FOR 1910.

The products of the clay-working industries in the United States—brick, tile, pottery, etc.—reached in 1910 the largest value ever attained, the total being \$170,115,974, compared with \$166,321,213 in 1909. These figures are presented by Jefferson Middleton, of the United States Geological Survey, in an advance chapter from "Mineral Resources" for 1910—"Clay-Working Industries."

In the brick and tile industry building brick of all kinds except fancy or ornamental declined in value, while drain tile, sewer pipe, architectural terra cotta, fireproofing, stove lining, and fire brick showed gains. In the pottery industry every item increased in 1910 except stoneware and yellow and Rockingham ware, which showed a loss of about \$200,000.

The imports of pottery increased but little and the proportion of domestic production to consumption, 77 per cent, was the highest ever recorded. Some idea of the growth of the pottery industry may be obtained from the fact that as late as 1875 the domestic production was but 15 per cent of the consumption. The exports of high-grade domestic pottery in 1910 showed a small increase, but the value of exports of all clay products increased over 31 per cent. The increase in the price of common brick was one of the most noteworthy features of the industry in 1910, the most marked example of this being in Illinois, where the price advanced from \$4.20 per thousand in 1909 to \$5.62 in 1910. The decrease of 570,353,000 in the common brick produced, however, caused a loss in value in this class alone of \$2,031,564. Every state and territory, except Alaska and Hawaii, is a producer of burned clay.

The following are the ten states with highest recorded production for 1910:

State.	Brick and Tile.	Pottery.
Ohio	\$17,231,236	\$14,294,712
Pennsylvania	19,814,355	2,279,930
New Jersey.....	9,245,854	8,588,455
Illinois	14,331,414	844,747
New York.....	9,778,288	2,093,661
Indiana	7,143,306	956,704
Missouri	7,058,705	29,061
Iowa	5,310,706	17,535
California	4,744,968	97,423
West Virginia.....	1,322,457	2,675,588

The rapid growth of the clay-working industries during the last 10 years forms an interesting study. The total value of these products increased from \$110,211,587 in 1901 to \$170,115,974 in 1910, a gain of 54 per cent. Fire brick attained its maximum value in 1910, with \$18,111,474, nearly doubling that of 1901. Drain tile showed a steady gain throughout the 10 years and in 1910 reached a value of \$10,389,822. Architectural terra cotta and fireproofing underwent but few depreciations in value during the period, and both reached their maximum in 1910, \$6,976,771 and \$5,110,597, respectively. Pottery also reached its maximum value, \$33,784,678, in that year. The highest value of common brick was reached in 1905, the fig-

ures for 1910 (\$55,219,551) being within 10 per cent of the maximum. Vitrified paving brick showed an almost steady gain, its maximum value, \$11,269,586, being reached in 1909, the value for 1910, \$11,004,666, being a slight decrease. Front brick doubled its value from 1901 to 1909, but the 1910 figures, \$8,590,057, showed a decline. Enamel brick also decreased in value in 1910, at \$832,225, after more than doubling its value from 1901 to 1909. Sewer pipe reached its maximum value in 1907, though the value of the 1910 production, \$11,428,696, shows but a small decrease. Tile, other than drain, after considerable variation, showed a large gain in 1909 at \$5,291,963, and a small decrease in 1910 to \$5,240,644.

THE USES OF PEAT.

The Federal Bureau of Mines has just issued a bulletin, "The Uses of Peat for Fuel and Other Purposes," which contains the results of an investigation that was undertaken to determine whether peat, a fuel widely used in some countries, could be servicable in the United States. The author of the bulletin, Charles A. Davis, the peat expert of the bureau, gives an exhaustive review of the entire problem, both in this country and in Europe, and draws the conclusion that the peat beds of this country are a great and neglected resource, which, when properly and fully developed, will add to our national wealth no inconsiderable quantity of good fuel and of raw material for important arts and manufactures.

Mr. Davis tells frankly about the good and bad of peat. He declares that the difficulties that have always been encountered in utilizing peat for fuel are due to the fact that in its natural state peat contains only about 10 per cent of combustible matter, the remaining 90 per cent, more or less, being water. He also says that in the last few years, more than \$1,000,000 has been spent in erecting plants and in experimenting with peat, and that these efforts were unsuccessful.

"Because the closing of larger plants before they had reached a stage of demonstrated success was so general," says Mr. Davis, "more conservative developments have been planned for making a thorough trial of the material in favorably situated places under American conditions of production and supply."

Mr. Davis estimates that there are more than 11,000 square miles of land in the United States having peat deposits of good quality. He declares that in these deposits there are 12,888,500,000 tons of peat with a value of more than thirty-eight billion dollars, enough peat to furnish heat and power for the entire country for many years.

The author is of the opinion that there will soon be a demand for peat as a fuel, at the same time he gives the following warning: "The foundation of all successful development and growth of peat industries in the United States must be a thorough scientific study

of the occurrence, nature, qualities and peculiarities of peat itself and a careful and honest investigation of the status of these industries in the European countries in which they have reached self-supporting existence. To begin without these preliminary studies would be the height of folly."

Mr. Davis says further: "It is an exceedingly interesting coincidence and a most important economic consideration that the regions where peat is most abundant are relatively remote from the coal fields, the only exception being the overlapping of peat and coal in Michigan. When one also notes that the more northern states, in which fuel is most needed, and the parts of the southern states where other kinds of fuel are not readily available, are rich in peat, it seems strange that a more careful examination into the possibilities of the peat resources of the country has not been made, because potentially they have large value and great possibilities.

"In conclusion, peat fuel may be said to be especially useful for certain purposes for which wood was formerly in general use and for which coal has not yet been altogether successfully introduced, such as brick and other forms of ceramic firing and lime burning. It appears to reach its highest value, however, as a source of producer gas in properly constructed gas producers.

"The fact must be noted that no quantity of peat fuel of any type sufficient to prove its value has yet been produced in the United States; until this has been done, although the outlook and European experience warrant further investigation of its possible uses and value, no final conclusions as to the commercial value of American peat as compared with coal can be reached."

Oil-shale lands in Moncton and adjoining counties of New Brunswick have been acquired by parties who purpose development on a large scale. Sir William MacKenzie of Toronto and his Canadian Northern associates have made extensive purchases of oil-shale lands. The plan is to expend about \$2,000,000 in the construction of a plant with retort and refining machinery, as used in the Scotch shale-oil fields, for the distillation of oil and securing the sulphate of ammonia and other by-products.

The great heaps of refuse to be seen adjoining coal and iron pits throughout Scotland, which have always been looked upon as useless waste product, are now being used in the manufacture of bricks. According to a consular report an industry has been started in Glasgow for the utilization of "coke breeze." This "breeze," mixed with Portland cement, produces a "fireproof partition," made in the form of slabs varying in size from 2 ft. to 3 ft. 6 ins. in length, and 1 ft. in breadth, and in thickness from 1 to 4 ins. These dimensions can be increased if specially desired.

APPARATUS FOR THE MANUFACTURE OF AQUA AMMONIA FROM SULPHATE OF AMMONIA.

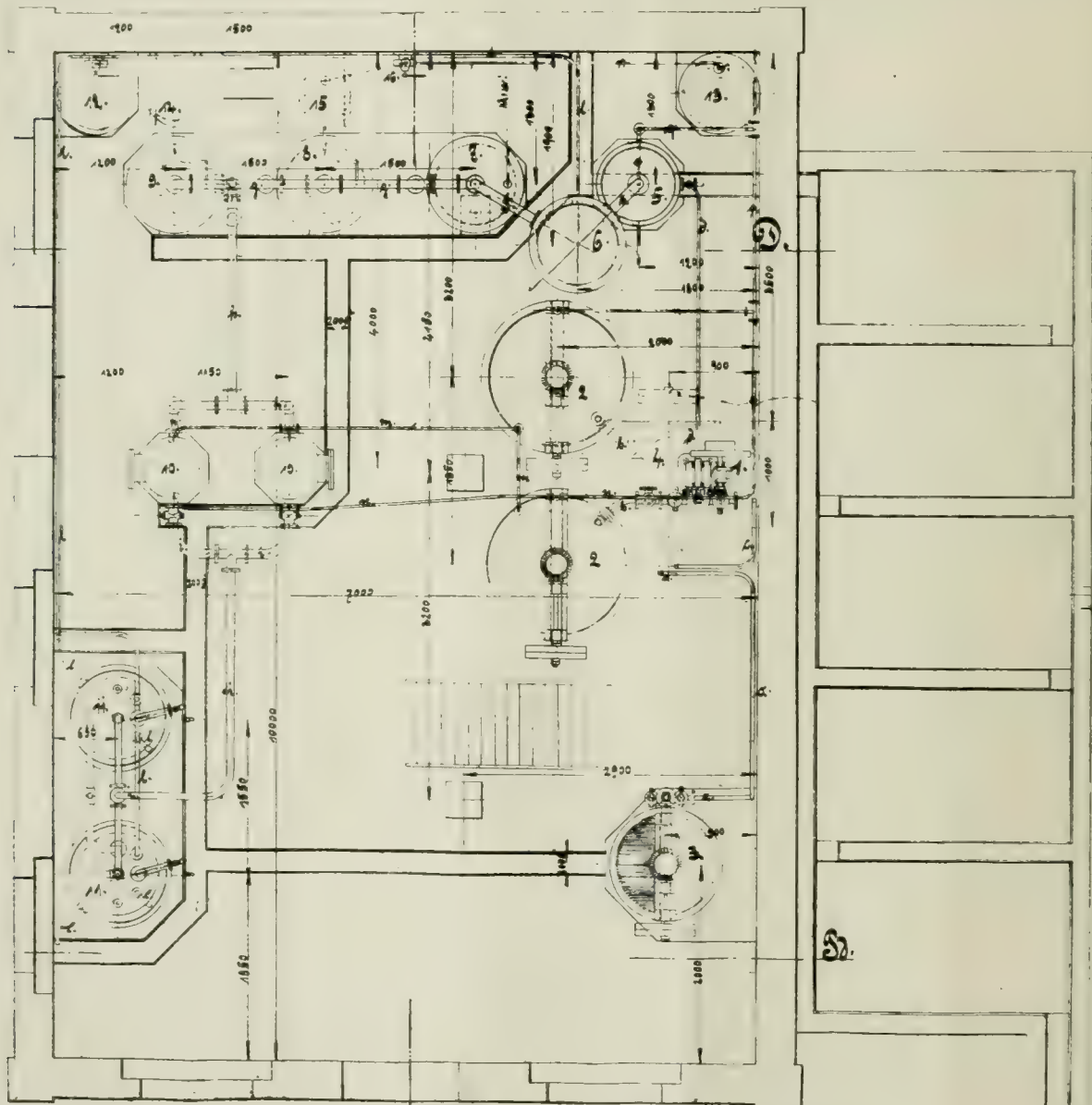
By R. W. HILGENSTOCK.*

The apparatus described below was designed by the writer and manufacturer in the works of E. Bendel, Magdeburg-Sudenburg, on a contract closed with E. Hartmann engineering-office at Wiesbaden. The apparatus is to be delivered to São Paulo, Brazil (South America). In as much as crude ammonia liquor from

gas works or coke oven plants could not be obtained, sulphate of ammonia had to serve as the raw material instead of the ammonia liquor. The following is a description of the process, the numbers in parentheses indicating the parts shown in the accompanying cuts.

The sulphate of ammonia is dissolved in the vessels (2) which are arranged with stirrers and so much water is added that the analysis of the solution will show about 1 per cent of ammonia (NH_3). By means of pumps (1) this solution is pumped into the decomposing vessel (4) where it comes in intimate contact with milk of lime, made in the cylindrical ap-

*Magdeburg-Sudenburg, Germany.



Plan of NH_4OH Plant Showing Arrangement of Apparatus.

BILL OF APPARATUS.

Object.

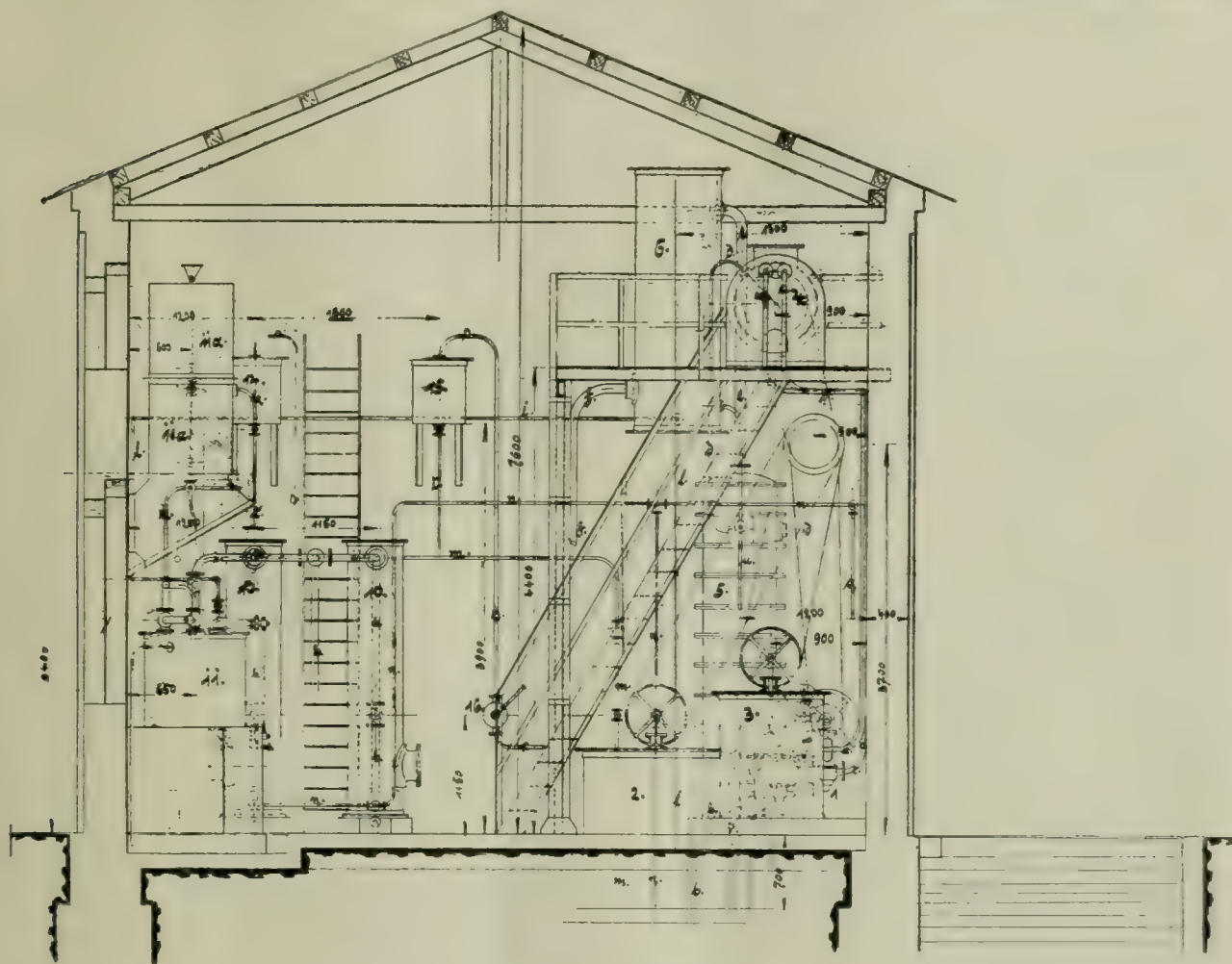
(1) Steam Pump with Power Connection to Cistern Apparatus; (2) Cistern in Which Materials Are Dissolved; (3) Cistern Used in Preparing Milk of Lime; (4) Cistern Used for Milk of Lime Reaction; (5) Ammonia Distilling Column; (6) Dephlegmator; (7) Ammonia-Water Washing Apparatus; (8) Caustic Soda Washing Apparatus; (9) Oil Washing Apparatus; (10) Filter; (11) Primary Absorption Apparatus; (11a) Secondary Absorption Apparatus; (12) Oil Tank; (13) Caustic Soda Cistern; (14) Oil Reservoir; (15) Caustic Soda Reservoir; (16) Pressure Pumps.

Pipe Lines.

(a) Line from Milk of Lime Tank to Reaction Tank, 40 litres sec.; (b) Line from Solution Kettle to Steam Pump, 60 litres sec.; (c) Line from Steam Pump to Reaction Tank, 30 litres sec.; (d) Line from Reaction Tank to Column, 40 litres sec.; (e) Line from Column to Dephlegmator, 80 litres sec.; (f) Line from Dephlegmator to the Washers, 70 litres sec.; (g) Connects the Washers, 50 litres sec.; (h) From Washers to Filters, 50 litres sec.; (i) From Filters to Absorption Apparatus, 50 litres sec.; (k) From Primary to Secondary Absorption Apparatus, 12-in. Gas Pipe; (l) Cold Water Pipe to Dephlegmator and Absorption Cisterns, 1½-in. Gas Pipe; (m) Exhaust Pipes from Filter to Solution Cisterns, 1-in. Gas Pipe; (n) Steam Lead for Filters and Solution Cisterns, 1½-in. Gas Pipe; (o) Steam Lead for the Steam Pump, ¾-in. Gas Pipe; (p) Exhaust Pipe for Steam Pump, 1-in. Gas Pipe; (q) Steam Lead for Distilling Column, 1-in. Gas Pipe; (r) Suction Piping for Pump; (s) Pressure Pipe for Pump, ½-in. Gas Pipe; (t) Piping from Caustic Soda and Oil Reservoir to the Washers; (u) Syphon Pipe for Condensed Water from the Dephlegmator.

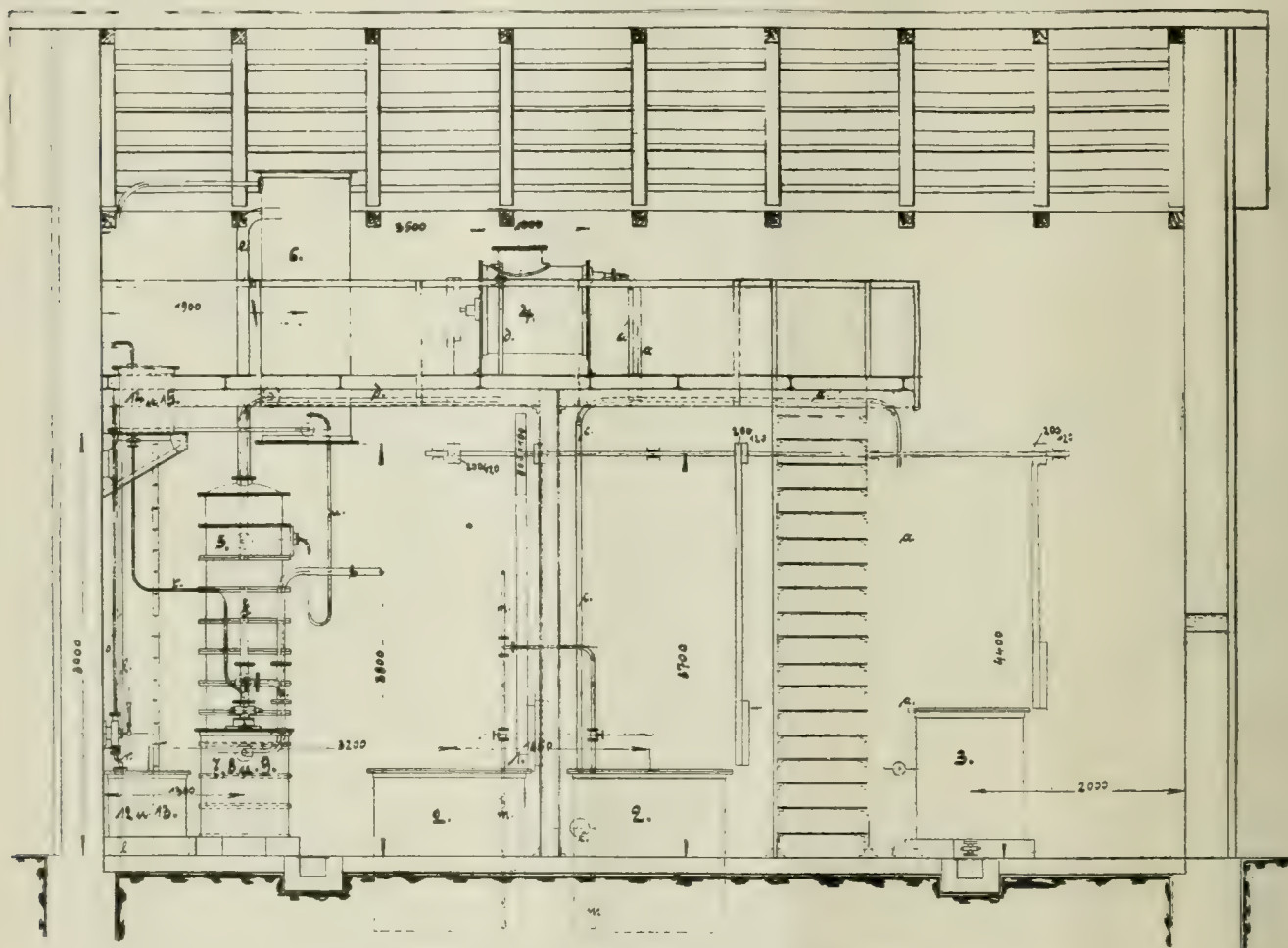
paratus (3). Inside of this tank a basket is provided for the lime stone to be slacked and by means of a stirring arrangement, driven by a pair of bevel gears from a horizontal shaft, not only the water but also

for this mixture is arranged on one of the high points of the cylinder and is connected with the upper section of the still (5). This apparatus equals in construction as well as in working, the stills which are



ammonia-gas enters is a water washer (7) of special design and supposed to keep back sulphuretted hydrogen, if there is any, and pyridine. For drying and further purifying purposes, an alkali-washer (8) of about the same construction as the water washer is placed and for finally retaining any oily substances an oil washer (9) is provided. The construction is similar to that of the previous two washers. The filling consists of a heavy tar or mineral oil, which holds back the small particles of light oils mechanically carried in the ammonia-stream. To retain the last parti-

absorbing takes place, preventing any loss of ammonia. After some hours, the water in the primary absorber (II_1) has absorbed sufficient ammonia to have the desired strength of the aqua ammonia, for instance a specific gravity of 0.910. When this point is reached, which can easily be determined by a hydrometer, the aqua ammonia is drawn off either in carboys or in wrought iron drums. After this the vessel is refilled again with the water, contained in the two compartments of the secondary absorber, which are filled again to one-third of their capacity



Longitudinal Section Through Center of Building.

cles of impurities and obnoxious odors, two wrought iron cylinders (10) filled with charcoal and bone-black serve as filters for the ammonia-gas, which, after it has passed these filters is now ready for the absorption in distilled water. To have the absorption go on in the right way (2) primary absorber (II) and one secondary absorber (IIa) are arranged. The first two absorbers have a water jacket as well as a cooling coil inside, while the secondary absorber is a cylindrical vessel, divided into two compartments without any cooling arrangement. The ammonia gas first enters the primary absorber (II_1), afterwards the primary absorber (II_2), then the lower compartment of the secondary absorber (IIa) and finally the upper section of this apparatus. Each compartment is filled about one-third with distilled water, so that quadruple

with fresh distilled water. The ammonia stream, however, is reversed; it passes first the primary absorber (II_2), then the primary absorber (II_1) and finally the two compartments of the secondary absorber (IIa_1) until the aqua ammonia in the primary absorber (II_2) has the required strength. After the finished product is drawn off, the water of the secondary absorber is filled again into the empty vessel, the secondary absorber filled again with fresh distilled water and the ammonia stream reversed and so on. The construction and arrangement of the absorbing apparatus is designed, that a product, containing up to 33 per cent (NH_3) can be made without any loss of ammonia, provided, however, that sufficient cooling water, having a temperature of about 18° Cels. can be used.

Before closing this article, I wish to state yet, that the pump (1₁) which pumps the ammonia sulphate solution into the decomposing vessel, has been so constructed that it drives the entire transmission, which is needed in the plant.

PLATINUM PRODUCTION IN 1910.

The entire output of crude platinum in the United States is recovered from placer mines in Oregon and California, which also produce gold.

In 1910, according to Waldemar Lindgren, of the U. S. Geological Survey, these mines produced 390 troy ounces of platinum, valued at \$9,507, against 673 troy ounces in 1909, valued at \$12,803. This decrease in value obviously does not represent the actual decrease, as the average price paid in 1910 was \$24.38 an ounce, compared with \$19 an ounce in 1909.

California's production in 1910 amounted to 338 troy ounces of crude platinum, valued at \$8,386. Of this total 304 ounces was recovered as a by-product in dredging operations in Butte, Yuba, and Sacramento counties. In Oregon the principal reported output comes from beach sands near Port Orford and near Bullards. The quantity recovered in 1910 was only 53 troy ounces, valued at \$1,121.

It is calculated that the domestic output of the crude metal from placers in 1910 is equivalent to 273 fine ounces of refined platinum.

The United States Mint obtains annually from its refinery operations a considerable quantity of platinum, the largest part of which is derived from scrap platinum and from sweepings, etc., bought from jewelers and dentists. A small percentage of primary metal is, however, obtained in refining gold bullion received at the mint from placer and lode mines. Private refineries also separate platinum from gold bullion. The best estimate that can be made as to what part of this output is derived from domestic sources, says Mr. Lindgren, would probably be about 500 fine ounces, which added to the refined platinum equivalent to the crude metal from domestic placers would give 773 ounces as the probable output of refined platinum from domestic ores in 1910.

A considerable quantity of refined platinum, estimated to be 4,800 ounces, valued at \$156,960, is produced from imported crude platinum, the largest part of which comes from Columbia and Russia. The total output of refined platinum in the United States, of both domestic and foreign origin, was about 5,573 fine ounces, valued at \$182,237.

During the last few years a large demand for platinum has developed in the jeweler's trade, especially for mounting precious stones but also for chains and other articles. This demand accounts to a great extent for the phenomenal rise in the price of the metal when the scarcity of the supply and the failure to discover new sources of production are considered. Platinum is also in strong demand for many industrial and chemical purposes.

DESIGN OF A 30-TON INDUCTION ELECTRIC FURNACE.*

By ALBERT HIORTH.

The design of this furnace has been based upon the data and results obtained with the original 5-ton furnace in Jossingfjord, Norway, as shown in the daily report sheets.

As the step from 5 tons to 30 tons is a rather large one, it was necessary to carefully study beforehand the different factors determining the design. The two most important things to be determined were the power-factor, and the energy required to keep the charge at the working temperature.

The power-factor depends almost exclusively upon the design of the furnace and the periodicity of the supply. With a given resistance in the bath, a certain current is necessary to produce the required temperature. As the bath consists of only one turn round the magnet, the secondary current is equal to the primary current multiplied by the number of primary turns per leg.

The voltage required to pass this requisite current through the primary winding may be divided into two component parts, viz., one required to overcome the ohmic resistance ("The Resistance"), and the other required to overcome the inductive resistance ("The Inductance").

These two factors determine the power-factor of the furnace. With a given inductance the power-factor increases together with the resistance, and with a given resistance the power-factor decreases as the inductance increases.

The total resistance may again be divided into three parts: First, the primary resistance which represents the loss in the primary coils; second, a very small part representing the loss in the iron-core; third, the secondary resistance representing the resistance of the bath, and which may be termed the useful resistance.

This useful resistance depends upon the following three factors: The conductivity of the iron at the working temperature of the furnace; the skin effect; the dimensions of the bath. The first of these factors will be dealt with later; the second, the skin effect, can be neglected for our purpose, as it may safely be assumed that its effect upon the total resistance will be the same, even if the sectional area of the bath is altered considerably.

The third factor, the dimensions of the bath, is, of course, the main one. If the skin effect is neglected, the resistance increases proportionally with the length of the bath, and decreases proportionally with the sectional area.

With a given periodicity the inductance depends upon two factors: First, the magnetic resistance, viz., the "reductance" of the iron-core; second, the magnetic leakage between the primary windings and the bath.

*Paper prepared for the 20th General Meeting of the American Electrochemical Society, in Toronto, Canada, Sept. 21-23, 1911.

†Kristiania, Norway.

The first of these may be neglected, as the magnetising current of the furnace without any charge is only very small.

The second one, the magnetic leakage, depends upon the total flux which passes round any one of the windings (the primary winding and the bath) without also passing round the other; in other words, upon the total flux which escapes through the annular spaces between the two windings.

If the radial width of both the bath and the primary coils remains the same, this flux is practically proportional to the total area of the space between the winding and the bath, and if the distance between these two be not altered, the flux is proportional to the circumference of the bath.

each leg at a temperature of approximately 180°C . is 0.003 ohm.

The weight of copper per leg, 840 kg.

The core is approximately 40 by 50 cm., giving an effective sectional area of 1,800 sq. cm.

The weight of the core is approximately 15 tons. The periodicity of the supply is 12.5 complete periods, corresponding to 25 alternations per second.

From the daily report sheets recording volts, amperes and kilowatts, taken at intervals of about half an hour and extending from the beginning of July until the middle of October, 1910, we have selected six at random, and from these plotted diagrams showing the readings as ordinates, with the time as abscissæ. Three of these diagrams are shown in

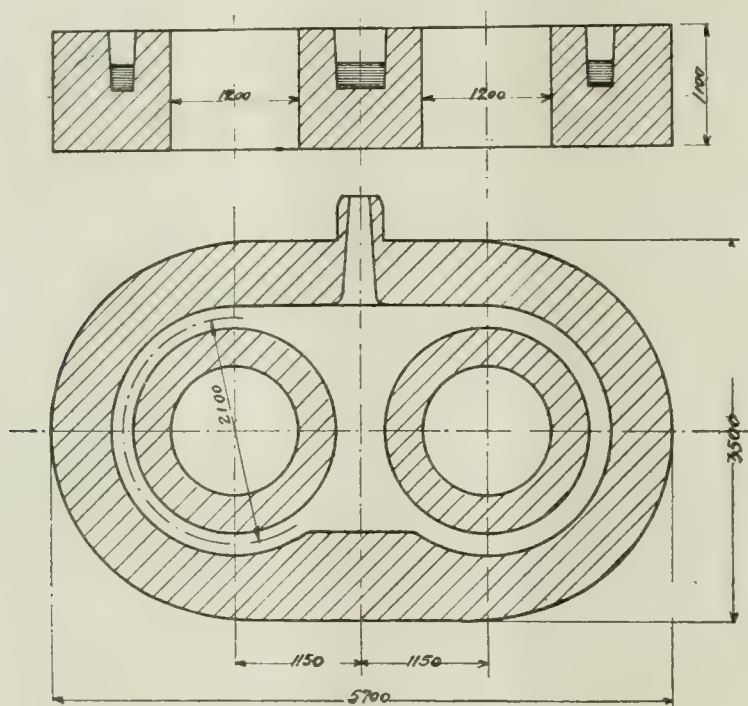


Fig. 1.—Sketch Showing Design of Furnace.

Consequently the inductance will increase with the diameter of the coils; if at the same time the radial width of the bath be increased, the inductance will be somewhat reduced again, but not nearly proportional to the increase in the width.

The inductance is also, of course, proportional to the periodicity, and may be lowered by using a lower periodicity. The influence of this will be more fully discussed later on.

The design of the present furnace is shown in Fig. 1. The data for the furnace are the following:

Mean diameter of the annular space occupied by the bath, 2.1 meters.

Width of this space, 20 cm.

Depth of the bath with a 5-ton charge, 27 cm. (specific gravity of the iron assumed to be 7).

The primary coils have 15 turns on each leg, 8 below and 7 above the bath. Each turn has a sectional area of approximately 1,000 sq. mm. The resistance of

Figs. 2-4. These are for the charges No. 45 (which was the charge witnessed by Professor Jos. W. Richards¹), No. 50 and No. 63. During the two first ones, pig iron was melted and converted into steel, whereas the last one was run for the purpose of refining low-grade steel.

In scrutinizing these curves, it will be found that the electrical conditions have varied considerably, and, in fact, more so than one is accustomed to expect in an induction furnace. This is partly due to the fact that the curves are plotted from actual readings on indicating instruments instead of being traced by recording instruments. In this way the peaks in the curves are naturally more pointed than would otherwise have been the case, and partly caused by the voltage of the generator being varied a good deal in order to alter the temperature of the bath.

Some of the peaks are evidently caused by the lifting

¹See Transactions American Electrochemical Society, 18, 204 (1910).

of the upper primary coils in order to gain access to the bath, either for inspecting purposes or in order to work the slag or to add material to the bath. An example of this last named disturbance is shown very clearly at 2.30 P. M. during charge No. 45. In this

tional area of the bath) and upon the disposition of the primary coils relative to the bath.

Considering the resistance first, this should, in accordance with the above theory, remain the same as long as the weight of the charge is the same. Apart

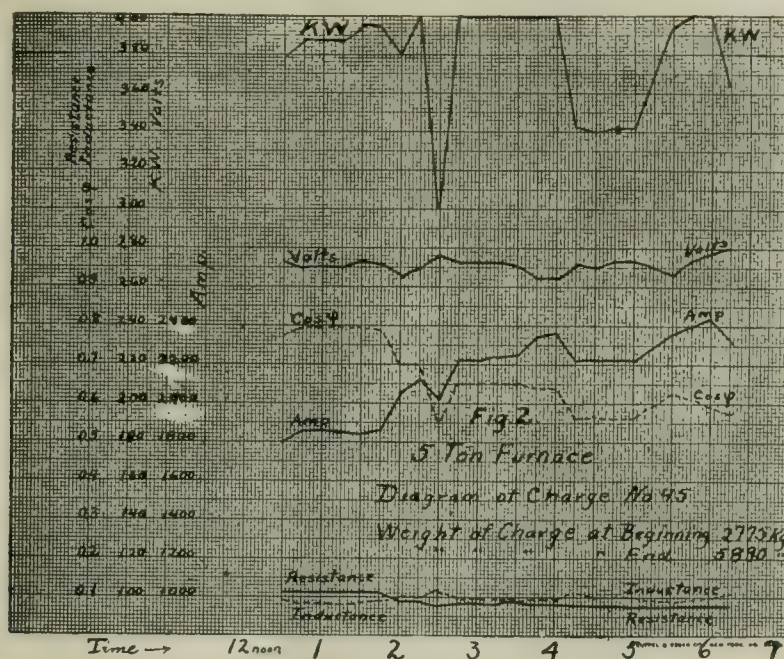


Fig. 2.—Diagram of Charge No. 45.

case the voltage has been kept constant and the inductance has been suddenly increased, due to the lifting of the upper coils. This causes a drop both in the amperage, the power-factor and the energy, although the voltage was not altered. These diagrams also show the variations in the power-factor, the resistance

from the variations caused by the adding of fresh material to the bath, there is, however, a marked decrease of the resistance as the process progresses; whether this is due to the alterations in the chemical composition, or whether the conductivity, after a certain temperature has been reached, begins to increase

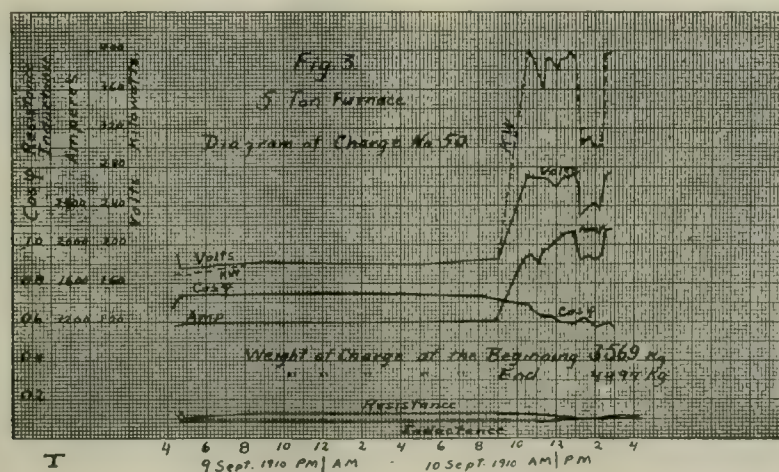


Fig. 3.—Diagram of Charge No. 50.

and the inductance. These last named have been arrived at by splitting the voltage up into its two component parts, and dividing these by the current. The results thus obtained represent directly the resistance and the inductance.

As has already been explained, the resistance and (with a given periodicity) the inductance are constants, which depend upon the dimensions of the bath, the weight of the charge (which depends upon the sec-

again with a further increase of temperature, cannot be stated definitely without further investigations.

This decrease of the resistance in the course of the run is shown very clearly on the diagram, Fig. 2, and also toward the end of the diagram, Fig. 3. In Fig. 4 this phenomenon is not observed, perhaps because this charge was only for refining purposes. It appears from the diagram as if the resistance was somewhat higher during the night, when the temperature was lower, but

as the inductance at the same time appears abnormally low, it is safer to assume that the readings, being at the lower part of the scale, are somewhat inaccurate.

If we consider only the resistance at the end of a

should be a straight line. In the diagram, Fig. 5, the points obtained are marked as dots, and the straight line drawn so as to represent the average of the readings.

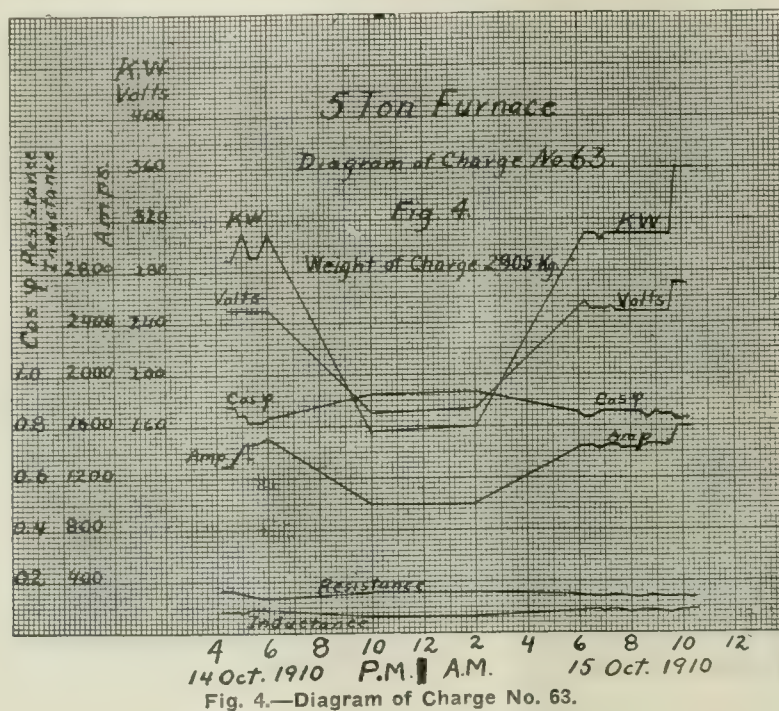


Fig. 4.—Diagram of Charge No. 63.

run or at the beginning, before fresh material is added, we obtain the following figures for the resistance from the reports analyzed:

Charge No.	Weight kg.	Sectional Area sq. cm.	Total Resistance Ohms.	Equivalent Useful Resistance Ohms.
8	1,475	160	0.390	0.380
8	5,032	545	0.094	0.086
29	2,532	273	0.128	0.120
29	5,878	635	0.066	0.058
41	3,600	390	0.124	0.116
41	5,764	623	0.070	0.062
45	2,775	300	0.125	0.117
45	5,890	630	0.070	0.062
50	3,569	386	0.125	0.117
50	4,497	485	0.088	0.080
63	2,905	314	0.140	0.132

The last column in this table gives the equivalent useful resistance, viz., the total resistance of the bath (twice the resistance of one ring) multiplied by the square of the number of primary turns.

In order to obtain this equivalent useful resistance, the total resistance has to be reduced by an amount corresponding to the resistance of the primary coils and to the losses in the iron-core. The resistance of the primary coils is 0.003 per leg = 0.006 for the whole furnace. The iron losses may be taken to represent the resistance equal to 0.002, corresponding to an iron loss of approximately 1-2 per cent, and the total of these will thus be 0.008. Subtracting these figures from the total resistance, we obtain the equivalent useful resistance given in the last column.

As the resistance varies in inverse proportion to the sectional area, the curve showing the relation between the section area and the inverse value of the resistance

In figuring the actual resistance from this curve, one obtains a specific resistance of the molten iron equal to 1.4 ohms per sq. mm. cross-section and m. length.

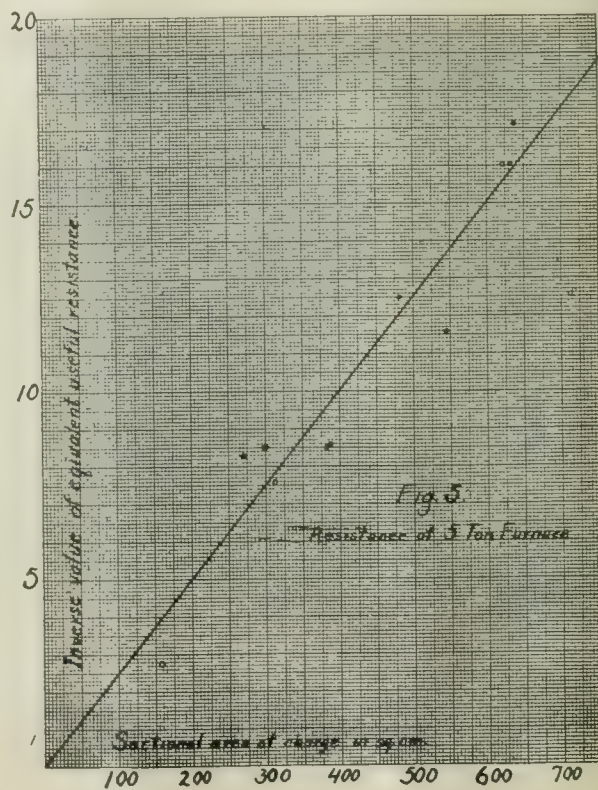


Fig. 5.—Diagram Showing Resistance.

In handbooks the value given is somewhat higher, and even as high as 1.7. The discrepancy may be due to inaccuracies, which are quite unavoidable, considering

the difficult nature of the measurements, or may be due to the fact that in our case the section of the bath is not absolutely uniform and that, for instance, the central portion of the bath, where the two rings meet, represents a somewhat lower equivalent resistance than the rest. The value 1.40, it must be remembered, includes all the irregularities in the shape of the bath, and also the skin effect, as far as this influences the resistance. It can only be used for figuring the resistance of furnaces of similar shape and disposition of the bath.

The inductance is independent of the weight of the charge, and remains constant at all times. It will be seen from the diagrams presented that the inductance varies between 0.09 and 0.10, except when the upper coil is lifted, and during the night (as in case of charge No. 63); but as the readings in this case, as already pointed out, are probably inaccurate, we may neglect

In order to increase the capacity of the furnace, it is necessary to increase the sectional area of the bath more than the length, as otherwise the diameter of the bath, and consequently the dimensions of the furnace, would become too large. The resistance of the bath will thus be considerably decreased, and at the same time the inductance will be increased, owing to the larger diameter, which increases the area of the space between the primary and the secondary windings.

The power-factor will thus in any case be reduced with the increased capacity, and we have figured that a 30-ton furnace built on the same line as the present one, for single-phase current, with a two-leg magnet and a current supply with 25 alterations, would show a power-factor equal to 0.25, and that the power-factor even with 15 alterations per second would still be only 0.38.

It was therefore decided by me that the 30-ton fur-

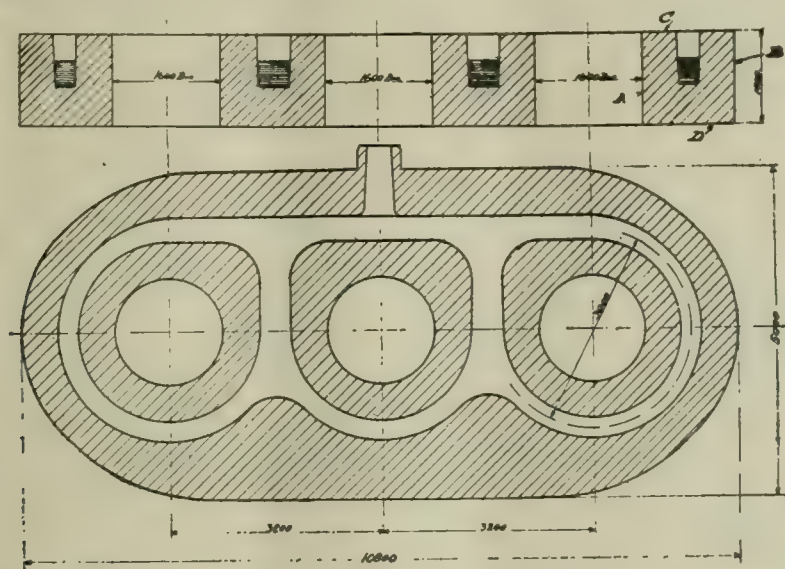


Fig. 6.—Sketch Showing Design of New Furnace.

this part of the diagram. All the other diagrams correspond to those shown, and the value of the inductance for the old furnace may therefore be taken as 0.095.

Using the figures thus established for the resistance and the inductance, we can figure out theoretically the power-factor of the present furnace with different charges, and obtain the following table:

With 3 tons	$\text{Cos. } \phi = 0.81$
With 4 tons	$\text{Cos. } \phi = 0.73$
With 5 tons	$\text{Cos. } \phi = 0.65$
With 6 tons	$\text{Cos. } \phi = 0.60$

As will be seen, this corresponds very well with the values given on the curves representing the different charges.

We are now in possession of the necessary figures to proceed with the design of the large furnace and to base it upon the experience with the old one.

With regard to this design, the first condition, of course, is that the space for the charge must be large enough to hold 30 tons, but the actual dimensions and shape of the bath must be such as to give the best possible power-factor.

nance should be built on the three-phase principle instead of the single-phase. In this case the weight of the charge per ring is only 10 tons instead of 15 tons with a single-phase furnace, and, as will be shown later, the reduction of the power-factor is not nearly so great.

In order to facilitate the tilting of the furnace, the three rings were disposed in one row. This arrangement is not strictly symmetrical, and it is to be expected that the load on the middle phase will be somewhat different from the load on the two outer ones, on account of the difference both in the inductance and in the resistance. With a special supply this is, however, not a very serious drawback, particularly as the difference between the phases in all probability will not be very great.

The dimensions finally chosen for the new furnace are shown in Fig. 6; from this we may now determine the resistance and the inductance in order to arrive at the power-factor.

Using the figure 1.40, the useful resistance figures out to be approximately 0.0001.

In order to arrive at the total resistance, this has to

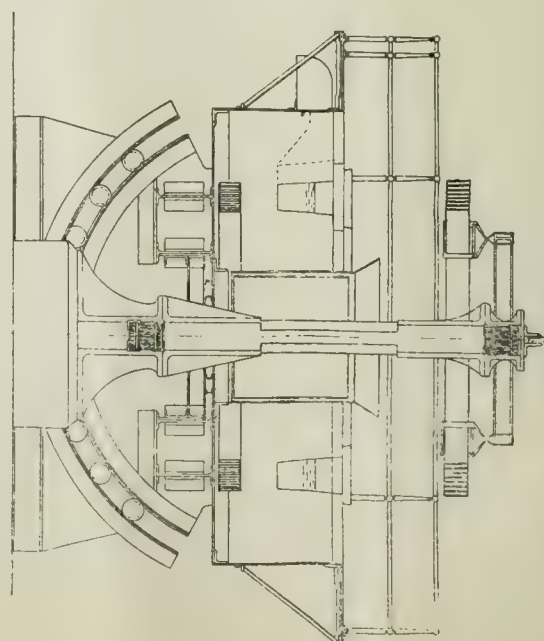
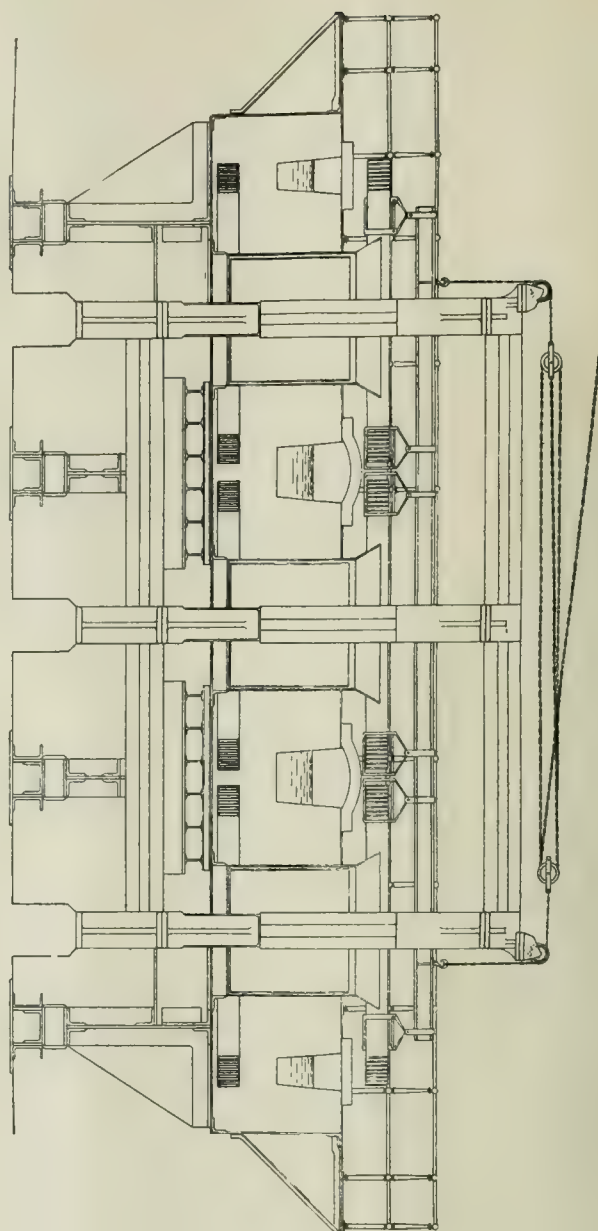
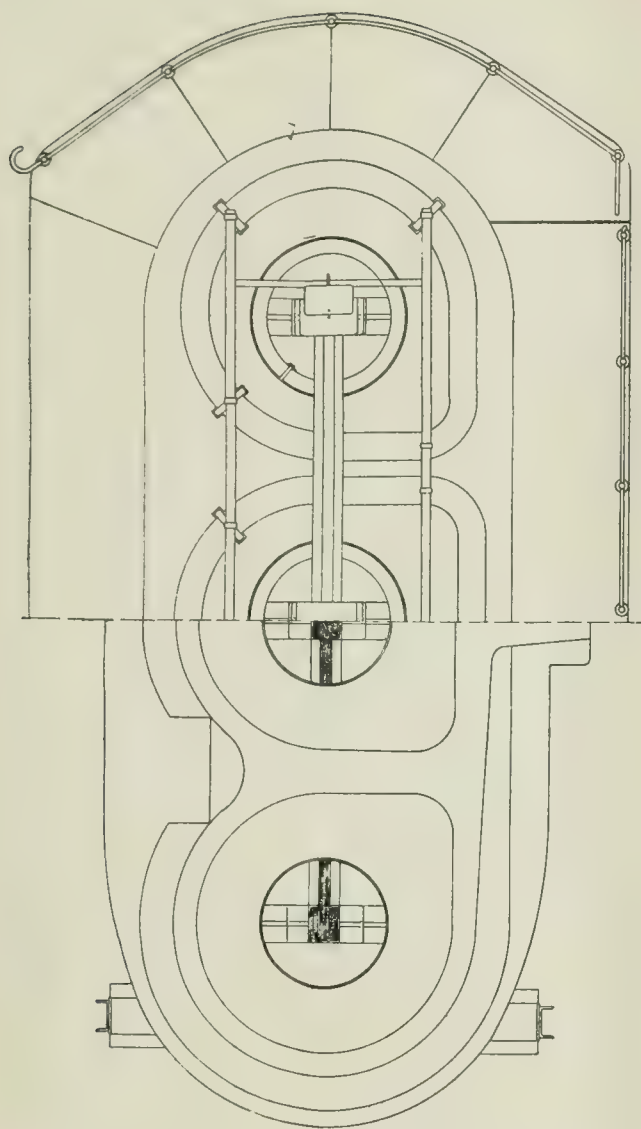


Fig. 7.—General Arrangement of 30-Ton Furnace.

be increased approximately 7-10 per cent on account of the losses in the primary winding and the iron-core, and the total equivalent resistance based on one winding becomes then 0.00011.

The inductance of the old furnace was 0.095, or, reduced, to one turn, 0.00021. In the new furnace this will be increased in proportion to the diameter, that is 0.00021×3

$$= 0.0003.$$

2.1

These values of the resistance and the inductance would give a power-factor equal to 0.34, which is still too low.

In order to increase the power-factor, it is necessary to further decrease the inductance by using a lower periodicity. What can be obtained in this way is shown in the following table:

Periodicity.	Power-factor.
25 alts.	0.34
20 alts.	0.41
16 alts.	0.50
10 alts.	0.67

From this table we select a periodicity of 16 alterna-

tions per second. To decrease the periodicity further still will hardly pay, seeing that the cost of the generator will thus be further increased, even if the output is reduced on account of the power factor being improved. This, however, is a matter which should be gone into more closely later on, in connection with the actual cost of the generator.

It remains to figure out the necessary energy required for the furnace, the dimensions of the iron-core and the number of primary turns, together with the sectional area of these.

As the furnace will be used with a liquid charge, and no melting-down will take place, the amount of energy required is only the amount necessary to keep

to keep the charge in a molten condition during the night was approximately 180 kw., and during the refining the energy varied between 250 kw. and 350 kw. The minimum energy required for the new furnace should consequently be $2 \times 180 = 360$, and the maximum, $2.5 \times 350 = 875$. We have assumed 700 kw., but at the same time the generator should be constructed in such a way that, by merely altering the voltage, it can give anything between 400 and 1,000 kw. With 700 kw. the current per ring becomes approximately 46,000 amperes, and the current density in the bath will be about 0.34 ampere per sq. mm.

The further data of the furnace, based upon the figures arrived at above, are:

No	Variations in		1 Min 2 Norm 3 Max			Cesf	Remarks.	
	Resistance	Inductance	Wt	K.W	Volts			Amp.
1	±0	±0	1	408	175	2700	0.5	
			2	700	228	3540		
			3	1000	275	4240		
2	-25%	±0	1	423	175	2840	0.58	The charge may be increased to 375 tons without reducing the power factor more than to .5. The max and min energy as well as current and voltage will then be the same as in the first case
			2	700	228	3160		
			3	1000	265	3800		
3	-25%	±0	1	349	175	2480	0.40	If the charge is reduced to 225 tons, the power factor will be .5 and the conditions again the same as in the first case
			2	700	228	3050		
			3	775	261	4200		
4	±0	+25%	1	288	175	2275	0.42	If the number of turns is reduced to 12 and the charge at the same time reduced to 24 tons, the power factor will be .5, and the max Energy 955 KW at 275 volts, 4000 Amp.
			2	700	273	3540		
			3	770	275	3570		
5	+25%	+25%	1	329	175	2170	0.5	By reducing the number of primary turns to 12, the max Energy may be increased to 955 at 275 volts, 4000 Amp. Power factor .5
			2	700	255	3160		
			3	815	275	3420		
6	-25%	+25%	1	234	175	2370	0.325	If the charge is reduced to 18 tons and the number of turns at the same time reduced to 12, the max Energy will be 955 KW at 275 volts, 4000 Amp. Power factor .5
			2					
			3	578	275	3725		
7	±0	-25%	1	611	175	3310	0.61	By increasing the number of turns to 15, the charge may be increased to 40 tons. The electrical conditions will then be as in the first case
			2	700	187	3540		
			3	1000	224	4230		
8	+25	-25%	1	628	175	3000	0.69	By increasing the number of turns to 15, the charge may be increased to 50 tons. The electrical condition will then be as in the first case
			2	700	184	3160		
			3	1000	221	3800		
9	-25	-25	1	530	175	3630	0.5	By increasing the number of turns to 15, the max Energy will be 1000 KW and the conditions otherwise the same as in the first case
			2	700	197	4090		
			3	770	207	4300		

Fig. 8.—Table Showing Electrical Conditions of 30-Ton Furnace with Varying Resistance and Inductance.

the bath at the required temperature. Apart from the small losses in the primary coil and the iron-core, all the energy is converted into heat in the charge itself, and, as soon as a constant temperature is reached, finally conducted to the surface of the furnace and given out from this by radiation, conduction and through the cooling arrangements. If the water-cooling is arranged in the same way and the amount of water increased correspondingly, it may therefore be assumed that the loss of heat, and consequently the energy required to keep the charge hot, will be in proportion to the surface of the furnace.

From Fig. 6 we determine the surfaces of the old and new furnace, as follows:

	New Furnace.	Old Furnace.
	Sq. m.	Sq. m.
Inside circular surface (A.)	20.5	8
Outside surface (B.)	35.	17
Upper surface (C.)	28.	17
Lower surface (D.)	28.	15

The surface of the new furnace is consequently between two and two and a half times as large as the old one. The amount of energy required in the old one

Iron core, 1,200 sq. cm. Weight, about 23 tons.

Primary windings; voltage, 230 volts.

Number of turns per leg, 13, disposed 7 below the bath and 6 above.

Sectional area, 2×20 cm.

Weight of copper for the whole furnace, about 13.5 tons.

As stated above, the theoretical number of turns is only 13, but in order to be able to run the furnace at full resistance should prove to be somewhat different from the values given, two turns should be added per leg, making the number of turns in the upper coils 8. The last three turns in each of these coils should be provided with terminals, enabling one to use at will 12, 13, 14 and 15 turns per leg.

In Fig. 7 is shown a general arrangement of this furnace, designed on the same lines as the old one. The lower coil is embedded in the masonry below the bath, and consists of copper tubes arranged for water-cooling. The upper coil may be lifted in order to inspect the bath.

The inner surface of the furnace, marked "A" on Fig. 6, is also arranged for water-cooling.

In order to keep the covers for the bath small, the channels were given the form shown in Figs. 6 and 7. The primary coils have been shaped accordingly to follow the shape of the bath as closely as possible.

The primary voltage has been fixed at about 230 volts, as this low voltage greatly facilitate the construction and the insulation of the windings. To embed the coil in the masonry of the furnace would, for instance, be impossible with a higher voltage, and also the upper coil would have to be built and cooled in quite a different manner if it had to carry high-tension current. The use of high-tension current would therefore necessitate a considerably increased distance between the bath and the coils, and thus a considerably lower power-factor.

The table below shows the principal data for the old furnace and the new one:

	Old Furnace.	New Furnace.
Total capacity.....	5 tons	30 tons
Capacity per leg.....	2.5 tons	10 tons
Diameter of bath.....	2.1 m.	3 m.
Width of bath.....	20 cm.	30 cm.
Depth of bath.....	27 cm.	45 cm.
Total surface of masonry	55 sq. m.	110 sq. m.
Total length of platform..	8¾ m.	13 m.
Total width of platform..	5¼ m.	6.5 m.
Sectional area of core per leg	1,800 sq. cm.	1,200 sq. cm.
Weight of core.....	15 tons	23 tons
Number of primary turns per leg.....	15	13 (see p. 12)
Sectional area of primary windings.....	1,000 sq. mm.	4,000 sq. mm.
Weight of copper per leg..	0.875 tons	ca. 4.5 tons
Total weight of copper...	1.75 tons	ca. 13.5 tons
Energy used.....	250 kw.	700 kw.
Copper losses.....	12.3 kw.	40 kw.
Iron losses.....	18 kw.	18 kw.
Power Factor.....	0.65	0.50
Voltage	250	230
Periodicity (½ alternations per second).....	12½	8
Amperes per phase.....	1,400	3,540
Kind of current.....	1 phase	3 phase

The generator should, according to the foregoing, be designed for a normal output of 700 kw., 8 periods (corresponding to 16 alternations) per second, 230 volts, 3,540 amperes, and a power-factor of 0.5. At the same time it must be able to give 400 kw. at 165 volts, and 1,000 kw. at 275 volts, with the same power-factor, and 290 and 125 kw., respectively, with a power-factor of 0.362. The maximum current will thus be 4,300 amperes.

The engine or turbine driving this generator should be for a maximum output of 1,550 effective h. p., and run at a practically constant speed at all loads between 600 h. p. and 1,550 h. p.

This plant should be quite sufficient to supply energy to the 30-ton furnace, even if the constants of this should vary considerably from the figures given above. In order to study this, we have prepared the table, Fig. 8, showing what would happen, and the maximum and minimum energy which could be supplied to the

furnace, in case either the resistance or the inductance or both should vary 25 per cent from the assumed value, either up or down.

This table shows the reason why the upper coils should be provided with connections, as these coils enable one to compensate for even quite considerable variations both in the resistance and the inductance.

A report of the United States Geological Survey states that the world's production of bauxite in 1909 totaled 270,581 tons valued at \$949,924, of which the American share was 128,099 tons worth \$251,188.

The Canadian Pacific Ry. has decided on using crude oil as fuel for its locomotives on the portion of its British Columbia division known as the Shuswap and Mountain sub-divisions. Circular tanks of riveted steel boiler-plate with a capacity for 200,000 gallons each will be constructed at several points. It is stated that the only change necessary in the locomotives will be the substitution of jet burners in the fire boxes. The tenders will be changed to hold oil instead of coal.

The U. S. Steel Corporation is to make a test of a miner's carbide lamp in its mines in the Marquette iron range. Providing the new device for underground illumination is found satisfactory it is understood that it will be adopted by the company for use at all of its Lake Superior properties. The test will be made at the Section 16 mine at Ishpeming. Tallow candles and oil lamps are now in general use. These furnish very poor light, yet for want of something better they have been doing duty ever since the inception of Lake Superior mining decades ago. Important advantages are claimed for the carbide lamp. It weighs less than an oil lamp or a candlestick and candle, it produces no smoke or odor and it reduces the fire danger to the minimum. It is substantially made of brass. The carbide lamp looks much like a pepper box, except that it has a headlight about 3 ins. in diameter. There are two sections, the upper one being used for water and the lower section for the carbide. The charge is sufficient to keep the lamp in commission two and one-half hours, at the end of which time the supply is renewed by changing the lower section for an extra one that the miners carry on their person. Both lower sections are recharged at the dinner hour. Properly used, the lamps will last for years. To induce good care of them, the company will charge a small price for the lamps, but one that will not represent the cost. The new device was introduced at the Republic mine of the Cambria Steel Co. a number of months ago and is said to have given satisfaction and to be very popular both with the men and the officials.

METALLURGY.

THE DETERMINATION OF COPPER—A MODIFICATION OF THE IODIDE METHOD.*

By E. C. KENDALL.

For the determination of copper the most important methods are the electrolytic, the iodide, and the cyanide. As the determination by means of the electrolytic method requires a considerable amount of time and apparatus, the only methods for the rapid estimation of copper are the iodide and the cyanide.

Upon an examination of the two volumetric methods mentioned it is apparent that in respect to the amount of time and attention required for a determination the cyanide has a great advantage over the iodide method. However, in respect to the accuracy of the results obtained the iodide method is conceded to be by far the more accurate of the two. As every consideration would be in favor of the iodide method if it could be modified in such a way as to make it as rapid and easy of manipulation as the cyanide method, an attempt was made to make such a modification.

In the determination of copper by the iodide method the copper may be originally present as copper, copper oxide, or sulfide. The first step is to obtain the copper in solution. Practically the only way to do this is to dissolve it in nitric acid. The solution of the copper with nitric acid produces nitrous acid in the solution, and it is the removal of this which causes the delay in the estimation of the copper. As the method is described in the literature, the nitrous acid is destroyed with bromine, the excess of bromine being removed by boiling; or the nitrous acid is removed by evaporating to dryness.

The modification of the iodide method as described in this paper consists in the destruction of the nitrous acid without boiling. This is accomplished by the addition of a small amount of sodium hypochlorite. The addition of sodium hypochlorite to a nitric acid solution produces hypochlorous acid. The interaction of hypochlorous acid and nitrous acid results in the oxidation of the nitrous acid and the formation of hydrochloric acid, and the reaction between hypochlorous acid and hydrochloric acid results in the destruction of the hypochlorous acid and the formation of free chlorine and water. As the solution of sodium hypochlorite contains small amounts of chlorides, hydrochloric acid will always be present when the solution is acidified, thus insuring the destruction of the hypochlorous acid and the formation of free chlorine. We thus see that the effect of adding sodium hypochlorite to the solu-

tion is the complete destruction of the nitrous acid and the formation of free chlorine.

To remove the free chlorine in solution some compound must be added which will take up the chlorine, but will not affect subsequent operations. Such a compound is found in phenol. Under the conditions of the determination, phenol will add chlorine directly to the benzene ring, but is not affected by iodine or any of the other compounds in the solution. Chlorophenol not being ionized removes all traces of free chlorine.

This modification of the method greatly reduces the time and attention required for a determination, and, in addition, the copper solution is prepared in such a way that iodine can be liberated by copper alone.

In the determination, the copper, copper oxide, or sulfide is dissolved in nitric acid. After the addition of the sodium hypochlorite and phenol, which requires but a moment, the solution is made slightly alkaline with sodium hydroxide, and is then made acid with acetic acid, when the solution is ready for titration. Potassium iodide and starch are added, and the titration is made to the disappearance of the starch iodide color. There is never any fear of the blue color "flashing back," and the solutions will remain colorless indefinitely after the titration. As the ionization constant for acetic acid is too low to allow nitrates to liberate iodine, the amount of nitric acid in solution is immaterial. Even 20 cc. of concentrated nitric acid will not affect the titration. However, too great an acidity is to be avoided, as nitrophenol will be formed. The presence of nitrophenol prevents the determination of copper, but there is no danger of its formation even in the presence of a large amount of acid if the solution is neutralized soon after the addition of the phenol. If a large amount of nitric acid is used to dissolve the copper, it should therefore be partly neutralized before addition of the phenol.

As chlorine easily oxidizes phenol to compounds which prevent the determination of copper it is essential that all of the phenol be added quickly to the solution. Under these conditions the chlorine adds directly to the benzene ring, but if the phenol is added drop by drop the chlorine will oxidize it, producing colored compounds in solution.

In order to add the phenol quickly enough to the solution it may be poured in from a beaker, or, a more convenient way, from a pipet from which the tip has been removed so that the delivery is from an opening which is of the same bore as the rest of the tube. By forcing the phenol out of such a pipet with the breath the entire volume is added very quickly and at the

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same time the phenol is well mixed with the contents of the flask.

After addition of the phenol the chlorine gas which is in the flask above the liquid is removed by blowing it out with the breath, and the sides of the flask are washed with a jet of water from a wash bottle. There should be no odor of chlorine just before the solution is made alkaline.

It should be remembered that the end point of the titration is not pure white. Cuprous iodide has a cream color, and when a large amount of copper is present the cuprous iodide gives a decided tint to the solution. When the end point is nearly reached a drop of the thiosulphate is allowed to fall into the center of the flask. If a change of color occurs the solution is given a slight rotary motion and after the solution is again quiet another drop of the thiosulphate is added. This "spot test" is easily recognized and gives a very accurate end point.

The speed of reaction of the copper with potassium iodide varies with the volume. In a small volume the action is rapid and all of the iodine is liberated at once, but in a large volume an appreciable time may be required for all of the copper to react. This is especially noticeable when a small amount of copper is present. A high concentration of potassium iodide greatly assists the liberation of the iodine. Accurate results can not be obtained unless at least 3 grams of potassium iodide are added, irrespective of the amount of copper present, up to 500 mg. of copper.

The solutions required are:¹

A. *The Sodium Hypochlorite* solution is made by boiling together a mixture of 112 grams of calcium hypochlorite and 100 grams of anhydrous sodium carbonate in 1,200 cc. of water. After the calcium is precipitated as carbonate, the solution is filtered and its strength found as follows: 5 cc. of the hypochlorite solution are added to 100 cc. of water containing 5 cc. of 30 per cent potassium iodide solution, and a few cc. of dilute hydrochloric acid are added. The liberated iodine is titrated with 0.1 *N* sodium thiosulphate. The volume of the solution is now adjusted so that 5 cc. of the hypochlorite solution are equivalent to 30 cc. of 0.1 *N* sodium thiosulphate.

B. *Phenol*.—A 5 per cent colorless solution of phenol.

C. *Sodium Hydroxide*.—A 20 per cent solution.

D. *Acetic Acid*, 50 per cent.

E. *Potassium Iodide*.—A convenient way to use this is to prepare a solution which contains 30 grams per 100 cc. of solution. Then 10 cc. will contain 3 grams, which is the amount needed for a determination.

F. *Sodium Thiosulphate*.—For the accurate titration of the liberated iodine two solutions are used. One strong solution, 1 cc. of which equals 6 mg. of copper, and a weak solution, 1 cc. of which equals 1 mg. of copper. The strong solution is run in until

the iodine liberated by the copper gives a light straw color to the solution. Starch is then added and the titration is finished with the weak solution.

As a thiosulphate solution loses strength, it should be restandardized from time to time. A convenient way to do this is as follows: A solution of sodium thiosulphate, approximately 0.1 *N*, is made by dissolving 24 grams of the crystallized salt per liter of water. After the solution has stood at least twenty-four hours it is standardized against copper by the method described below. Pure electrolytic copper which has been cleaned with emery paper should be used. After dissolving 150 to 200 mg. of the copper in 6 to 8 cc. of 50 per cent nitric acid the solution is treated as described below and the thiosulphate is then standardized with this known weight of copper. The most convenient means of restandardizing the thiosulphate is to use a solution of acid potassium iodate. Acid potassium iodate has the formula $\text{KIO}_3 \cdot \text{HIO}_3$, so that a normal solution has one-twelfth the molecular weight in grams per liter. A 0.1 *N* solution is prepared by dissolving 3.249 grams of the salt in 1 liter of water, and it is standardized against a known strength of thiosulphate as follows: Add 10 cc. of the acid iodate solution to 150 cc. of water containing 0.5 to 1 cc. of hydrochloric acid. Upon the addition of potassium iodide, iodine will be liberated according to the equation:



Starch is added and the titration is made to a colorless solution. From this titration the weight of copper to which 20 cc. of this solution are equivalent is accurately determined. A 20 cc. pipett is passed through a one-hole stopper and is allowed to remain in the acid iodate bottle. The end of the pipett is closed with a small rubber stopper. The exact copper equivalent of a thiosulphate solution is now easily found by titrating 20 cc. of the acid iodate solution whose copper equivalent is known with the thiosulphate as described above. The acid iodate remains constant indefinitely.

G. *Starch for Indicator*.—The best preparation for this purpose is a 0.5 per cent solution of Kahlbaum's soluble starch. This is prepared as ordinary starch, but gives a perfectly clear solution which is very sensitive with iodine. If ordinary starch must be used it should be free from all cloudiness.

DETAILED DESCRIPTION OF THE METHOD.

If the copper to be determined is present as metallic copper, 200-300 mg. are placed in a 300 cc. flask and dissolved in 5-10 cc. of 50 per cent nitric acid.

If the copper is present as cuprous oxide, it is filtered on a Gooch crucible through asbestos. The cuprous oxide is then dissolved through the Gooch crucible with 10-15 cc. of 30 per cent nitric acid into a 300 cc. Erlenmeyer flask.

If the copper is in the form of sulphide, it is filtered on a Gooch crucible which has a layer of asbestos one-eighth inch in thickness. The crucible is then placed in a small beaker of 50 cc. capacity, and 10 cc. of

¹The weights given here are for calcium hypochlorite having 35 per cent or more available chlorine.

50 per cent nitric acid are added. The beaker is placed on a hot plate, and the nitric acid allowed to boil until all the black sulphide has gone into solution. The crucible is then washed off, and the solution transferred to a 300 cc. Erlenmeyer flask. The presence of the asbestos in the solution does not interfere with the titration of the copper.

If the copper to be determined is already in solution as sulphate, chloride, or other salt, sufficient solution is taken to give 100 to 300 mg. of copper.

Having obtained the copper in solution, preferably in a 300 cc. Erlenmeyer flask, the volume being between 50 and 60 cc. the acidity is adjusted to equal 4 to 5 cc. of concentrated nitric acid. A greater volume or acidity is to be avoided. The temperature should not be above 25°. Five cc. of the hypochlorite solution are now added to the copper solution, which is well mixed with a rotary motion. As soon as the color of the copper solution changes from a clear blue to a greenish tint, sufficient hypochlorite has been added. Another indication of a sufficient amount of hypochlorite is the liberation of chlorine. For weights of copper up to 200 mg., 2-3 cc. of the hypochlorite are sufficient. For larger amounts of copper more hypochlorite may be needed, but 5 cc. will be sufficient for any amount of copper which would be determined by this method. The reactions between the hypochlorous and nitrous acid require an appreciable time and the best results are obtained by allowing the solution to stand about 2 minutes before the addition of the phenol. This, however, is not essential. Ten cc. of the phenol solution are now added as quickly as possible, by blowing the solution from a pipet from which the tip has been removed.

The chlorine gas which remains in the flask above the liquid is removed by blowing into the flask and the sides are washed down with a jet of water. If the solution is allowed to stand at this point, nitrophenol will slowly form. Sodium hydroxide is therefore added until a very slight precipitate is obtained. The solution is now made acid with acetic acid; only a few drops should be required to dissolve the precipitate. Ten cc. of the potassium iodide are added and the titration made with the standardized thiosulphate. If great accuracy is required the titration is finished with a weak solution of thiosulphate.

The following are some results obtained by the method described above. The milligrams found and the error are calculated only to a point which is within the degree of accuracy of the apparatus used.

DETERMINATION OF COPPER.

Copper taken. Mg.	Copper found. Mg.	Error. Mg.	Error. Per cent.
20.00	20.01	+0.01	+0.05
20.00	19.99	-0.01	-0.05
20.00	20.00	-0.00	0.00
30.00	29.99	-0.01	-0.03
30.00	30.00	-0.00	0.00
40.00	39.98	-0.02	-0.05
40.00	39.96	-0.04	-0.10
60.00	60.01	+0.01	+0.02
60.00	60.01	+0.01	+0.02

Copper taken. Mg.	Copper found Mg.	Error, Mg.	Error, Per cent.
80.00	80.12	+0.12	+0.15
80.00	80.03	+0.03	+0.04
80.00	79.98	-0.02	-0.02
80.00	79.98	-0.02	-0.02
100.00	100.00	0.00	0.00
100.00	99.99	-0.01	-0.01
120.00	119.95	-0.05	-0.04
140.00	140.00	0.00	0.00
160.00	160.00	0.00	0.00
160.00	160.00	0.00	0.00
180.00	180.00	0.00	0.00
180.00	180.00	0.00	0.00
200.00	200.00	0.00	0.00
200.00	199.9	-0.1	-0.05
203.2	203.2	0.00	0.00
220.2	220.1	-0.1	-0.05
240.0	240.0	0.00	0.00
240.0	240.2	+0.2	+0.08
261.6	261.6	0.00	0.00
280.0	280.0	0.00	0.00
280.0	280.3	+0.3	+0.10
300.0	300.1	+0.1	+0.03
320.0	319.9	-0.1	-0.03
320.0	319.9	-0.1	-0.03
340.0	340.0	0.00	0.00

Note.—The sum of the + and — errors very nearly equals zero.

For the opportunity of carrying out this work I wish to thank Dr. N. B. Foster and for assistance with the analytical work Mr. A. W. Thomas.

In the last sitting of the Council of Ministers of Russia, a project was discussed providing a new method of exploiting the Government salt resources. It is proposed to let out the Government sources of salt by competition and to lengthen the term of lease.

The production of pig iron in Japan during 1910 has been estimated by the Department of Finance at 71,963 tons. In 1901 the amount was 32,455 tons, and the average production for the last 10 years is 50,000 tons. During 1910 the importations amounted to 117,227 tons, of which 98 per cent was received from Great Britain, while iron ore was imported to the extent of 208,190 tons, of which China supplied 61 per cent, Korea 35 per cent, and Great Britain 3 per cent.

Announcements of the discovery of potash in the United States always attract much attention in Germany, and a recent announcement of this sort brought forth a statement from the German Potash Syndicate that it had at once caused inquiry to be made by an expert official and found that the efforts of both the United States Geological Survey and the Department of Agriculture have thus far failed to locate any valuable potash beds. The newspaper report was declared to have been based on the well-known but unimportant potash beds in Death Valley. The Potash Syndicate puts little faith in the production of potash from the kelp of the Pacific coast, declaring that its production, except as a by-product of iodine, would not pay. The general press was not so skeptical, however, and referred to the news as at least a warning that Germany's natural monopoly in the potash field is not so certain for the future as has been supposed, and that it must so organize itself as to be ever ready to meet new competition.

HEAT TREATMENT OF A NICKEL STEEL.*

By W. CAMPBELL† AND H. B. ALLEN.††

Nickel steel has received a good deal of attention, notably by D. H. Browne¹ and A. L. Colby.² Stoughton, in his "Metallurgy of Iron and Steel," states that 3.5 per cent of nickel added to carbon steel will increase the elastic limit nearly 50 per cent, while reducing the ductility by only 15 to 20 per cent. About 3.5 per cent of nickel will give steel approximately six times the life in resistance to fatigue. Under the head of "Nickel Steel—Forging Quality," the following figures are given:

Composition: C, 0.25 to 0.3; Mn, 0.5; Ni, 3.2 per cent.

Elastic limit: 49,270; 57,300 lb. per sq. in.

Tensile strength: 87,360; 77,800 lb. per sq. in.

Elongation in 2 in.: 34; 31.5 per cent.

Reduction of area: 58; 62 per cent.

Guillet,³ in a paper on "Steels Used for Motor Car Construction in France," gives the following figures:

Nickel per cent	Carbon per cent	Condition.	Tensile strength, Tons.	Elastic limit, Tons.	Elongation per cent.
1-2	0.3-0.4	As rolled	31.75-38	20-24	27-20
		Quenched at 800° C	44.5	57	35
		Annealed at 500° C	44.5	57	35
			35	41	21.5-25.5
3.25-3.5	0.2-0.25	As rolled	54	66	42
		Quenched at 800° C	54	66	42
		Annealed at 500° C	54	66	42
			54	66	42

Waterhouse⁴ studied the heat treatment of a series of steels with 3.8 per cent nickel and 0.41 to 1.52 per cent carbon, and found that they behaved the same as ordinary carbon steels as regards temperature and microstructure. Overheating was quite perceptible between 1100° and 1200° C. As compared with ordinary carbon steels, the critical points, Ar₁₋₃, are 20° lower for each per cent of nickel.

Souther⁵ recommends for a steel of 3.3 to 3.6 per cent nickel, 0.2 to 0.3 per cent carbon, and 0.5 to 0.8 per cent manganese, the following heat treatment: "After forging, heat to 844° C. and quench in oil. Reheat to 426° to 537° C. and cool slowly."

In an annealed condition, this steel will have an elastic limit of about 60,000 lbs. per sq. in. and a reduction in area of over 50 per cent. After heat treatment an elastic limit of 90,000 lbs. per sq. in. and a reduction in area of over 50 per cent is obtained. This strength can be increased by quenching in water or in brine and by varying the drawing temperature. It is possible to obtain an elastic limit of 120,000 lbs. per sq. in. with at least 40 per cent reduction of area. The endurance of steel so treated, under vibration or

alternate stress, is at least ten times that of a steel in an annealed condition.

The material used in the present research was open-hearth steel, containing carbon, 0.27; nickel, 3.15; manganese, 0.65 per cent; rounds, 5/8-in. diameter; cold drawn. The investigation included:

1. Determination of critical points and of refining temperature (by microstructure).

2. Heating to various temperature from 600° to 1350° C. and cooling (a) in air; (b) in furnace; (c) by quenching in water; (d) by quenching in oil.

3. Heating to temperature giving maximum strength when quenched (900° C.) and (a) quench in water; (b) quench in oil, then draw at 200° to 660° C. and cool in air.

The physical properties, elastic limit, tensile strength, elongation in 2 ins., and reduction of area, were determined under (2) and (3), and the microstructure of the series was compared.

DETERMINATION OF CRITICAL POINTS.

A piece of steel of 5/8-in. diameter and 1 in. long was used, with a small hole drilled to center. The time was recorded by stop-watch and the temperature by a platinum-platiniridium couple and Siemens-Halske galvanometer. The heating was done in an electric furnace.

Ac₁ begins 670° C.; maximum 695° C.
Ac₂₋₃ begins 725 ; maximum 750. Ends 780° C. (?)
Ar₃ begins 795 (?) ; maximum 760.
Ar₂ begins 725 ; maximum (705) 660.
Ar₁ begins 630 ; maximum 590.

To check the point Ac₂₋₃, or the refining temperature, a piece of steel was heated to about 1300° C. and cooled in the furnace. Prices were reheated to 680°, 710°, 720°, 750°, 790° C., etc., and slowly cooled. Under the microscope the piece heated to 720° still showed traces of overheating, while that heated to 750° was refined. The piece heated to 790° showed a coarser grain.

Hence we may say that Ac₂₋₃ is complete at 750° C. which is about 75° lower than for ordinary carbon steel.

HEAT TREATMENT.

The test bars were heated in a gas forge, using a double iron muffle to insure uniform heating. The temperature was controlled by a thermo-couple inclosed in a quartz tube. The time of heating was from 35 to 50 minutes, and the bars were held at the maximum temperature for five minutes to insure uniform conditions. The furnace was then opened and three bars were withdrawn; one was cooled between two bricks in air, another was quenched in about 30 gals. of water at room temperature, and the last was quenched in oil. The furnace was then closed and the fourth bar allowed to cool there.

In Table I are given the physical properties of the bars heated to various temperatures and cooled in air. At the bottom of the list is No. 16, the steel as re-

*Read before the American Society for Testing Materials, June, 1910.

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††Met. E., Columbia, 1911.

¹Transactions, American Institute of Mining Engineers, Vol. XXIX, 1899, p. 569.

²"A Comparison of Certain Physical Properties of Nickel and Carbon Steel," 1903. Bethlehem Steel Company.

³Journal, Iron and Steel Institute, 1908, II, p. 177.

⁴Proceedings, American Society for Testing Materials, Vol. VI, 1906, p. 247.

⁵Society of Automobile Engineers, 1910.

ceived. Reheating to 700°C , i. e. above Ac_1 , decreases the elastic limit as shown in No. 16₁₁, while the increase in elongation is very marked, as we should expect. The next heat, No. 16₁₄, to 750°C . (Ac^{2-3}), gives the maximum ductility. At 1200°C . (No. 16₂₉)

TABLE I.—BARS HEATED TO DIFFERENT TEMPERATURES AND COOLED IN AIR.

No.	Cooled in air from $^{\circ}\text{C}$.	Yield point, lb. per sq. in.	Ultimate strength, lb. per sq. in.	Elongation in 2 in. per cent.	Reduction in Area, per cent.
16 ₁₁	700	66,630	90,370	33.3	62.8
16 ₁₄	750	67,400	89,500	37.5	64.4
16 ₁₇	800	63,600	89,000	34.5	50.5
16 ₂₀	900	59,660	86,500	35.0	58.7
16 ₂₃	1,000	58,240	87,840	33.0	59.7
16 ₂₆	1,100	59,000	88,300	32.5	60.5
16 ₂₉	1,200	71,740	93,340	25.0	42.3
17 ₄₉₋₂	1,250	63,360	93,400	22.5	35
17 ₄₇₋₂	1,300	69,700	95,500	...	36.2
17 ₄₈₋₂	1,350	77,200	98,400	10	11.5
16	as received.	83,170	93,175	22	58.7

there is a marked increase in strength and a corresponding falling off in ductility. This becomes very marked at 1350°C . (No. 17₄₈₋₂).

In Table II are given the physical properties of the

TABLE II.—BARS HEATED TO DIFFERENT TEMPERATURES AND COOLED IN FURNACE.

No.	Cooled in furnace from $^{\circ}\text{C}$.	Yield point, lb. per sq. in.	Ultimate strength, lb. per sq. in.	Elongation in 2 in. per cent.	Reduction in area, per cent.
16 ₃₆	610	71,650	91,100	32.6	61.0
16 ₁₂	700	60,350	86,700	36.0	59.0
16 ₁₅	750	61,400	86,700	39.5	58.8
16 ₁₈	800	...	85,300	37.0	54.8
16 ₂₁	900	53,240	84,710	34.5	59.5
16 ₂₄	1,000	52,490	85,760	33.0	55.1
16 ₂₇	1,100	51,650	84,400	35.0	59.4
16 ₃₀	1,200	51,390	83,800	35	54.9
16	as rolled.	83,170	93,175	27	58.7

bars cooled in the furnace. Heating to 610°C . (No. 16₃₆) lowers the elastic limit and increases the ductility, because heat treatment even below the critical points has marked effects on the properties of material that has been worked cold. As before, heating to 750°C . gives the most ductility, but even the 1200°C . heat shows little difference, showing that slow cooling may mask overheating.

The physical properties of the bars quenched in water are given in Table III. The sharp jump be-

TABLE III.—BARS HEATED TO DIFFERENT TEMPERATURES AND QUENCHED IN WATER.

No.	Quenched from $^{\circ}\text{C}$. in water.	Yield point, lb. per sq. in.	Ultimate strength, lb. per sq. in.	Elongation in 2 in. per cent.	Reduction in area, per cent.
16 ₃₈	610	81,300	101,000	27	54.5
16 ₃₇	665	72,370	94,480	25.5	64.0
16 ₃₉	680	67,240	103,950	...	...
16 ₃₉	700	136,900	153,200	...	14.0
16 ₃₈	750	197,000	211,200	2.5	4.4
16 ₃₈	800	223,000	223,000	1.0	2.4
16 ₃₈	820	146,450	230,650	2.0	4.5
16 ₃₈	850	139,100	162,800	...	...
16 ₄₀	870	168,360	275,800	3.0	7.0
17 ₄₃₋₁	895	...	252,300	2.5	4.1
16 ₃₈	900	112,200	233,800	...	...
17 ₃₈	900	159,380	268,150	2.0	7.9
16 ₃₄	900	118,200	253,780	2.5	5.3
17 ₄₄₋₁	925	...	245,200	4	6.8
16 ₄₁	945	206,400	265,000	2.5	5.5
16 ₄₀₋₁	980	...	228,500	2	3.7
16 ₂₃	1,000	147,500	164,300	0.0	4.4

17 ₄₆₋₁	1,000		252,000	6.5	...
16 ₂₅	1,100		230,900	...	...
16 ₂₈	1,200		234,000	...	...
17 ₄₉₋₁	1,250		155,000	0	4.9
17 ₄₇₋₁	1,300		96,400	...	1.0
16	as rolled.	83,170	93,175	27	58.7

tween No. 16₃₈ and No. 16₁₀ shows that at 700°C . Ac_1 has been passed, thus confirming the other determinations. The maximum tensile strength of 275,800 lbs. per sq. in. occurred in the bar heated to 870°C . (No. 16₄₀). The tensile strength remains high to 1200°C . heat. The results on quenched bars are liable to vary and are uncertain, as seen by comparing the three heats to 900°C . This is due in part to the slight set formed in the quenched bars at times. However, there are enough data to show that the strength does not fall off immediately above the maximum, as has been asserted.

Table IV gives the physical properties of the bars quenched in oil. The tensile strength is high, but somewhat below that of the water-quenched bars. The elastic limit shows a falling off, which may be accidental.

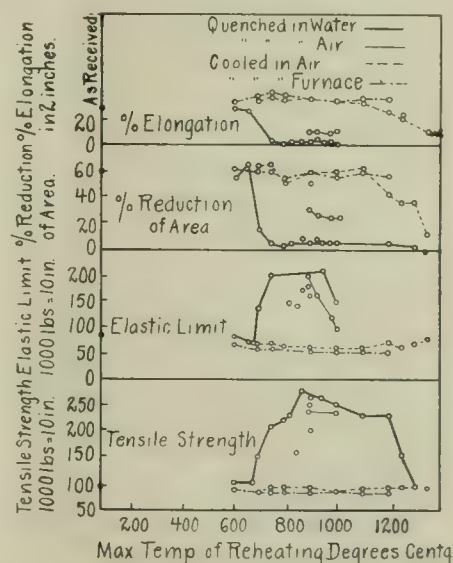


Fig. 1.

Bar 17₂₄ quenched at 900° shows such an abnormal reduction of area that it cannot be correct. It is probable that it was taken from the oil too soon. Bar 17₄₃₋₂ is therefore taken as the standard in Table VI.

TABLE IV.—BARS HEATED TO DIFFERENT TEMPERATURES AND QUENCHED IN OIL.

No.	Quenched from $^{\circ}\text{C}$. in oil.	Yield point, lb. per sq. in.	Ultimate strength, lb. per sq. in.	Elongation in 2 in. per cent.	Reduction in area, per cent.
17 ₄₃₋₂	895	197,300	236,000	10	29
17 ₂₄	900	161,400	202,730	12.5	51.2
17 ₄₄₋₂	925	162,800	229,300	10	26
17 ₄₅₋₂	980	119,700	231,400	8.5	23.6
17 ₄₂₋₂	1,000	99,200	235,200	10.0	24.2

REHEATING TESTS.

The next part of the work was the reheating of quenched bars; and the question arose as to the best temperatures for the initial quenching. Looking over the results shown in Fig. 1, we see that there is

marked similarity between the air- and furnace-cooled bars as regards tensile strength and elastic limit, the air-cooled in general being the stronger. This fits in with carbon steels generally. The ductility of the furnace-cooled bars is just a little greater, but the difference in all properties is not so marked as in carbon steels.⁶ The falling off at 1200° C. shows overheating.

In regard to the quenched bars, Ac_1 is well marked on the tensile-strength curve and by the drop in ductility at 700° C. The upper point, Ac_{2-3} at 750° C., would be expected to show nearly the maximum strength and minimum ductility. The elastic limit of this heat is high, but the maximum for tensile strength is at 870° C. This is most probably due to the rate

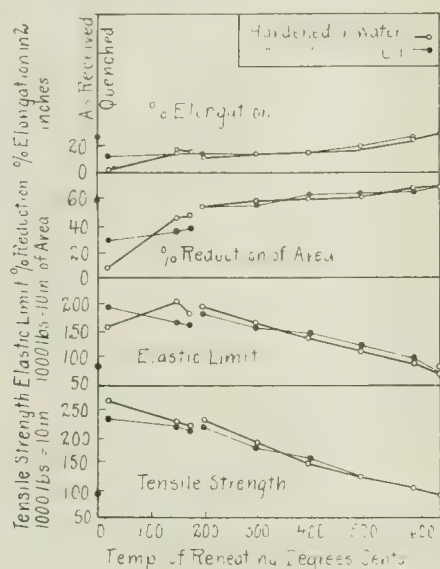


Fig. 2.

of cooling in the quenching process. It may be that we have to heat well above the critical point to get the maximum effect.

In regard to the best temperature for initial quenching of the material to be tempered, the choice lay between just above Ac_{2-3} , say 760° C., and 870 to 900° C., where the maximum strength was obtained. The latter temperature was chosen because, among other reasons, the grain would be much coarser than at 760°, whence the process of tempering could be followed more easily in studying the microstructure.

Six bars were heated to 900° C., quenched in water, then reheated to 200°, 300°, 400°, 500°, 600° and 650° C. in an electric furnace, and finally cooled in air. The time of tempering was about 45 minutes at maximum temperature. Six bars which had been quenched in oil from 900° C. were similarly treated. The figures for the two sets are given in Tables V and VI, and plotted in Fig. 2.

Water-Quenched and Tempered.—The original quenching gives a low ductility, elongation 2 per cent, reduction in area about 8 per cent. Reheating to 200° C., while it lowers the strength increases the elongation to 12 per cent, and the reduction in area to 54

per cent. In order to find whether tempering was effective at much lower temperatures, two more pairs of bars were heated to 900° C., quenched, and drawn to 150 and 175° C. These are bars 17₂₃₋₁ and 17₂₃₋₇ water-quenched and 17₂₄₋₈ and 17₂₄₋₇ oil-quenched. Having thus been quenched in another heat, these bars are not strictly comparable with the other six of the series. However, while maintaining a high tensile strength, the ductility is increased enormously by

TABLE V.—BARS HEATED TO 900° C., QUENCHED IN WATER AND REHEATED TO VARIOUS TEMPERATURES.

No.	Reheated point, to —° C.	Yield point, lbs. per sq. in.	Ultimate strength, lbs. per sq. in.	Elongation in 2 in., per cent.	Reduction in area, per cent.
17 ₁	0	159,380	208,350	2	7.9
17 ₂	150	206,000	230,000	15	45
17 ₃	175	183,500	219,600	15	47
17 ₄	200	196,000	233,500	12	54.0
17 ₅	300	166,140	189,070	14	58.8
17 ₂₃₋₁	400	139,700	153,730	15.5	59.9
17 ₂	500	112,580	126,690	19	62.7
17 ₃	600	91,815	105,160	26	68.5
17 ₄	650	70,300	93,760	30	65.0
16	as received	83,170	93,175	27	58.7

reheating to 150° C. These results are so remarkable that the work will be repeated with a series tempered between 100° and 200° C.

Oil-Quenched and Tempered.—Table VI shows the

TABLE VI.—BARS HEATED TO 900° C., QUENCHED IN OIL AND REHEATED TO VARIOUS TEMPERATURES.

No.	Reheated point, to —° C.	Yield point, lbs. per sq. in.	Ultimate strength, lbs. per sq. in.	Elongation in 2 in., per cent.	Reduction in area, per cent.
17 ₁	0	197,300	236,000	10	29
17 ₂	150	167,700	221,500	14	35
17 ₃	175	161,500	217,000	15	38
17 ₄	200	183,450	221,580	14.5	54.6
17 ₂₄₋₁	300	159,630	184,150	14	55.7
17 ₂	400	142,900	157,750	16	61.6
17 ₃	500	117,070	128,470	20	62.9
17 ₂₄₋₁	600	98,820	106,140	25	67.8
17 ₂	650	72,920	94,640	30	68.9
17	as received	83,190	93,175	27	58.7

effect of quenching in oil and reheating. The results are not so markedly different as in Table V, but from 200° C. the effect of reheating is uniform. At 650° C. we get back almost to the original steel, with a little more ductility. Fig. 2 shows these results graphically, and the uniformity above 200° C. indicates that the effects of tempering vary uniformly with the temperature.

From the above results we may pick the following for comparison with other material:

No.	Heated to 900° C. and quenched.	Reheated to —° C.	Yield point, lbs. per sq. in.	Ultimate strength, lbs. per sq. in.	Elongation in 2 in., per cent.	Reduction in area, per cent.
17 ₁	in water	200	196,000	233,500	12	54
17 ₂₄	in oil	200	183,450	221,580	14.5	54.5

MICROSTRUCTURE.

The structure of this steel shows the same variation of ferrite and pearlite as normal low-carbon steel. The quenched material, however, is more difficult to etch. The best results on quenched and tempered material were obtained with 2 per cent nitric acid in

⁶W. Campbell: Proceedings, American Society for Testing Materials Vol. VII, 1907, p. 240.

alcohol, followed by a slight repolish to get rid of the stain.

The overheated material is clearly seen to be refined at 750° C., which is at a much lower temperature than for a corresponding carbon steel.⁷

Quenching at 700° C. gives a fine-grained mixture of ferrite and austenite (martensite), while by quenching at 750° we have nothing but martensite. The higher the temperature above this, the coarser the grain. Tempering, of course, has no effect on the grain size, but effects the austenite (martensite) itself, decomposing it more and more, therefore making it etch more and more deeply. In other words the change yields pseudomorphs after austenite; the higher the temperature of reheating the more extensive the decomposition. Lastly, some recent work on the effect of time of tempering shows that at 300° C. there is a marked difference between tempering for a half hour and for 18 hours. This work is to be continued.

Table VII gives the principal changes in microstructure:

TABLE NO. VII.—STRUCTURE OF NICKEL STEEL AFTER VARYING TREATMENTS.

No.	Treatment.	Microstructure.
16	As received	Fine grained mixture of ferrite and pearlite. Outside shows more ferrite and effect of cold drawing.
16.0	Heated to white, cooled in furnace	Coarse grain. Characteristic overheated structure.
16.8	Heated; reheated to 680° C.	Pearlite refined (?). Ferrite unrefined.
16.7	" " " 710	Almost refined. A little coarse ferrite remains.
16.9	" " " 720	A trace of coarse ferrite unabsorbed.
16.6	" " " 750	Refined completely.
16.5	" " " 790	Grain slightly coarser than last.
16.4	" " " 810	Grain slightly coarser than last.
16.2	" " " 820	Same.
16.1	" " " 850	Grain coarser.
16.3	" " " 885	Grain coarser. A few large grains.
17.22	" " " 900	Same.
17.10	Heated to 700° and quenched	Fine grains of ferrite in austenite.
17.13	" " 750 " "	Very fine grained martensite.
17.16	" " 800 " "	Slightly coarser martensite.
17.33	" " 850 " "	Slightly coarser martensite.
17.19	" " 900 " "	Much coarser martensite.
17.44	" " 1,018 " "	Coarser martensite.

CONCLUSIONS.

A steel with 3.15 per cent nickel, 0.27 per cent carbon, and 0.65 per cent manganese, may be refined by heating to 750° C., which is about 75° lower than for an ordinary carbon steel.

Hardening is complete when quenched from this temperature, but higher tensile strength was obtained by quenching around 900° C.

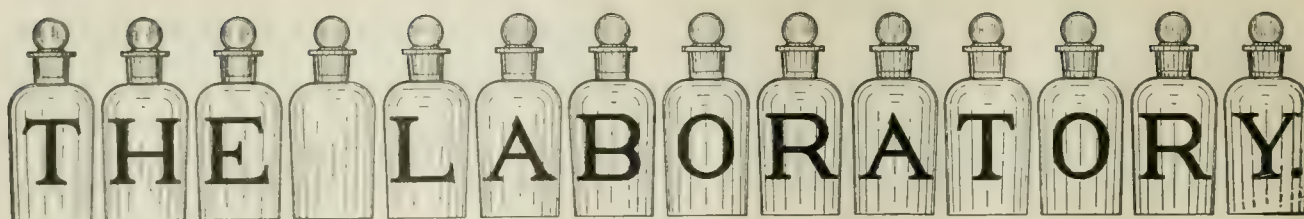
Overheating becomes marked above 1200°.

Tempering of bars quenched in water or oil gives very uniform increase in ductility and decreases in strength, the change varying very uniformly with the temperature of reheating, till at 650° C. the properties are very nearly those of the original steel, having a slightly lower elastic limit and greater reduction in area.

It is announced by the Mines Department of the Canadian Government that the associated manufacturers at Brantford, Ont., have become so convinced that the air-dried peat method employed by the mines branch can be made a commercial success that they have contracted with the Government to continue the work at Alfred, Ontario, and will spend over \$50,000 of private capital in trying to improve peat machines. This action was decided on only after a thorough investigation. The machine to be used will have a capacity of 60 to 80 tons per day, as compared with the 30 tons the Government turned out. The Government experimental plant at Alfred exhibited samples of machinery and of peat ready for market at the Ottawa fair. One thousand tons of peat were made up, which was sold at \$3.25 a ton. The orders came with such a rush that the supply was soon exhausted. The peat was used in parlor grates, in kitchen ranges, and in furnaces. It burns to a fine ash, there being practically no residue, and is much cheaper than coal.

The different estimates of the beet-root crop as drawn up by the Russian Government institutions interested in this question are often at first greatly at variance. They are still further at variance, generally speaking, with the private calculations made by the association of sugar boilers. This year these estimates agree to a marked extent. Thus the official compilation from the data sent in by the inspectors of indirect taxation gives the 1911 harvest of beet root at 14,342,110 tons, while private calculations of the sugar boilers make it 14,380,533 tons. According to the latter, the total production of sugar in Russia will amount to 2,003,738 tons for the season of 1911-12. Adding to this the surplus brought over from the 1910-11 campaign, which amounts to 476,330 tons, the total quantity of sugar in Russia for 1911-12 will be 2,480,068 tons. The sugar-boiling factories will have to deal with a somewhat larger quantity of beets during the 1911-12 campaign than last year (when the total crop amounted to 14,227,982 tons), and will obtain rather less sugar, since the roots contain this year an average of 21.17 per cent of sugar against an average of 21.88 per cent in 1910-11. In other respects the roots are quite satisfactory. Up to the present time sugar-beets culture has been confined practically to the southern Provinces of Russia, but experiments made in Finland tend to show that favorable results may be had in the northern Provinces as well.

⁷W. Campbell: "Further Notes on the Annealing of Steel." Proceedings, American Society for Testing Materials, Vol. X, 1910, p. 193.



A MODIFICATION IN THE DETERMINATION OF MALIC ACID.

The accurate method for determining malic acid offered by Dunbar and Bacon¹ presents some difficulties in manipulation. These, briefly, are the slowness with which the various liquids filter and the great difficulty in always obtaining solutions sufficiently clear and free from small particles for polarizing. The lead salts have a tendency to pass through the filter, especially with certain types of fruit of low acidity.

The chief cause of this slow filtration is the presence of pectin bodies, always present in fruit juices to a greater or less extent. They rapidly clog the pores of the paper, and if present in sufficient amount will entirely stop the flow. Dilution helps the filtration, but introduces errors, especially when the malic acid content is originally low. The whole difficulty is avoided by other preliminary treatment, which is described in a recently issued circular of the United States Bureau of Chemistry. The circular was prepared by David S. Pratt, Assistant Chemist, Division of Foods.

A weighed amount of juice, generally 100 grams, is placed in a 500 cc. beaker. With vigorous stirring about two or three times the volume of 95 per cent alcohol is added. This throws out the pectin bodies, usually in such a form that after standing a few minutes they may be gathered into a coherent mass. The liquid is decanted through a filter and the precipitate washed twice with 95 per cent alcohol. The combined filtrates are then evaporated in a current of air on the water bath to about 75 cc. After cooling, the solution is made up to 100 cc. in a measuring flask, using 10 to 15 cc. of 95 per cent alcohol and distilled water. The temperature when the volume is finally made up to the mark should be close to that at which the polariscope readings are to be taken. This solution is then treated exactly as in the original method, except that no clarification is necessary. No difficulty will be experienced in filtering, as the liquid passes rapidly through the paper and has no tendency to clog.

The addition of alcohol in making up to volume has a twofold purpose. Lead malate is less soluble in an alcoholic solution, and the necessity of cooling with ice to remove it completely is, therefore, avoided. The chief advantage, however, lies in the fact that the lead salts of fruit acids are thrown out in the alcohol-containing liquid as gelatinous precipitates

which filter quickly and never cause trouble by passing through the paper unless a large excess of lead acetate has been used in the precipitation. This should always be avoided by adding it in small amounts with vigorous shaking after each addition until a few crystals remain unchanged at the bottom of the flask. When the powdered anhydrous sodium sulphate is added to remove the excess of lead the same advantage is noted. In this case without the alcohol even more trouble is encountered in obtaining a filtrate entirely clear and free from small particles that render it very difficult to polarize. With the alcohol, one or at most two filtrations give a water clear solution that may be read in a 200 mm. tube.

With that part of the solution containing the uranyl acetate a liquid is obtained which filters rapidly and can always be read in a 100 mm. tube. In cases where the alcohol has caused some fruit color to pass into solution the addition of a tiny drop of bromin and vigorous shaking and filtering, if necessary, before reading will give satisfactory results.

The modification has been thoroughly tested in the routine analysis of a large number of fruit samples. By this means, for instance, the thick mass resulting from crushed bananas may be handled. Here the malic acid content is rather low, and the solution would have to be so diluted in order to handle it in the ordinary way that the errors would be relatively large.

Another advantage of this method of procedure is that concentration of the original juice is possible. Two hundred grams may be used, and the final volume after evaporation made up as usual to 100 cc. With juices containing but little malic acid this is a great advantage, which could not be utilized in the original method. The time required to precipitate the pectins, filter, and evaporate off the alcohol is more than compensated for by the time saved in filtering the solution, and the use of longer tubes in the polariscope increases the accuracy of the method.

An application has been made to the Minister of Finance of Brazil for permission to work and export the guano which is found in large quantities on various uninhabited islands on the Brazilian coast, including those of Queimadas (large and small), Figueira, and Graca. The petitioner agrees to pay a percentage to the treasury on the sum received by him for his goods.

¹U. S. Dept. Agr. Bureau of Chemistry Cir. 76.

1. U. S. Dept. Agr. Bureau of Chemistry Cir. 76.

RAPID DETERMINATION OF SULPHURIC ACID WITH THE POROUS CLAY CRUCIBLE.*

By FREDERICK KLEIN, PH. D.

Every chemist in general will agree that up to the present our methods of gravimetric, and volumetric analysis are apt to have some phase where the accuracy is in doubt, where the reaction is not fully, or in some cases purely hypothetical, and therefore not absolutely correct; we therefore go through journals and chemical literature to find our way out of a labyrinth of reactions which take place by a simple precipitation of two bodies chemically acted upon according to the laws which govern these reactions, visible and obscure, to all our scientific endeavors, methods, instruments, ability and chemically reasoning.

One of the methods which is of the greatest importance and in practical use all over the chemical world

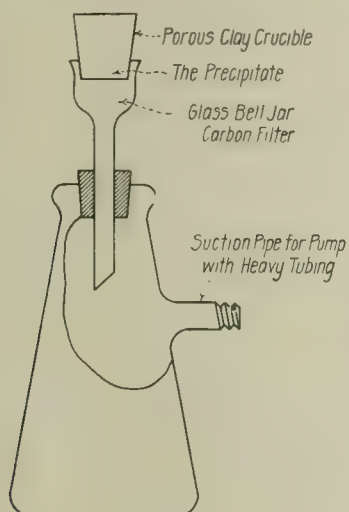


Fig. 1.

is the sulphur determination by barium salts, the considerable time and ability spent to perfect this one method alone would fully prove the correctness of the statement above. In one of the latest *Chemical News*, the prime and most distinguished German chemical paper *Chem. Ztg.*, No. 135, of Nov. 12, on page 1201, we read an article: again stating that the problem of the absolute precipitation of the sulphuric acid with barium salts is still problematic and requires considerable skill and comparatively an absurd length of time to obtain concordant and satisfactory results.

I therefore with pleasure can state, that through the aid of technical progress we have succeeded and obtained a most charming chemical device in the form of a porous clay crucible manufactured by a firm in one of the New England States, and therefore an American production of the highest esteem, and importance to the chemist, because it fully eliminates the filter paper process, which is one of the most objectionable features in most of the chemical procedures and analytical work of all kind, every chemist will welcome this

porous crucible because we all know the difficulty in burning filters, in regard to the ashes and at last; but not least, the reducing action of the carbon of the fiber which is highly objectionable, especially in the sul-

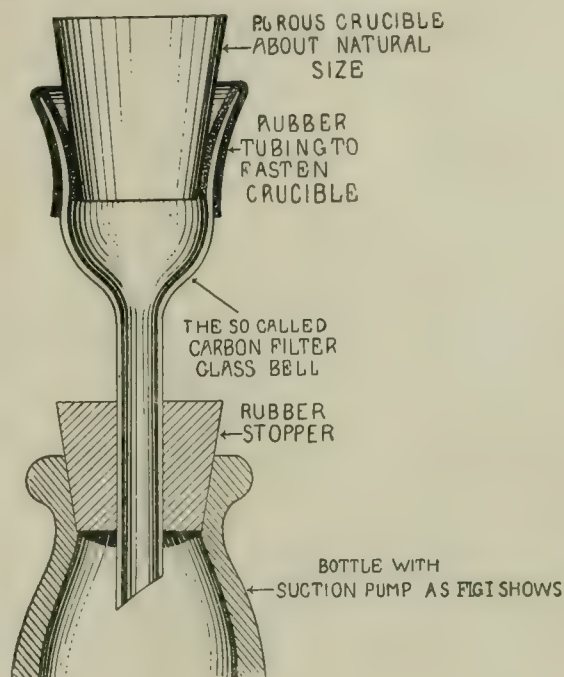


Fig. 2.

phur determination. These and many other objections which are daily observed in regard to these methods have led me to devise a new porous crucible which enables the chemist to make a dozen or even more sulphur determinations in comparatively the same length of time spent to make a single filter determination con-

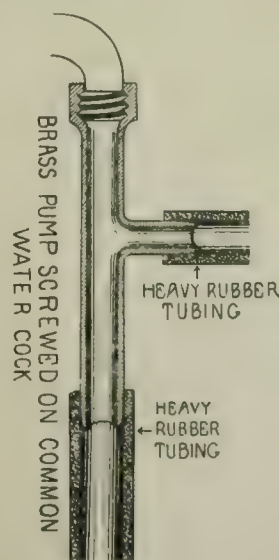


Fig. 3.

sidering all points of importance in regard to boiling and addition of barium salts, etc.

Taking the advice of "Hintz" and "Weber" in their extensive study of this especial method, if we operate under the same caution and condition, there arises one and the same inaccuracy which can be tolerated in this

*From the American Journal of Pharmacy.

method and by the other methods and greatly increase the accuracy after all.

I therefore describe this most simple and rapid determination of sulphuric acid, taking normal sulphuric acid as a standard with 49.0 gm. of H_2SO_4 to the liter: 10 cc. of $\text{N}/1 - \text{H}_2\text{SO}_4$ are transformed from a burette or pipette to a beaker of 300 or 400 cc., the acid is then diluted with three or four volumes of

NORMAL SULPHURIC ACID.

Factor 0.137 = for sulphur.

Interpolation table between 9 c.c. and 11 c.c.

$\text{BaSO}_4 = 233.5$

$\text{H}_2\text{SO}_4 = 49.05 = 98.1$

ccm of $\text{N}/1 \text{H}_2\text{SO}_4$ contains	BaSO_4	ccm of $\text{N}/1 \text{H}_2\text{SO}_4$ contains	H_2SO_4 in 1000 c.c.
9.0 c.c.	1.05075	9.0 c.c.	0.44145
9.1 "	1.062425	9.1 "	0.446355
9.2 "	1.07410	9.2 "	0.451260
9.3 "	1.085775	9.3 "	0.456165
9.4 "	1.09745	9.4 "	0.461070
9.5 "	1.109125	9.5 "	0.465975
9.6 "	1.12080	9.6 "	0.47088
9.7 "	1.132475	9.7 "	0.475785
9.8 "	1.14415	9.8 "	0.480690
9.9 "	1.155825	9.9 "	0.485595
10.0 "	1.16749	10.0 "	0.49050
10.1 "	1.179175	10.1 "	0.495405
10.2 "	1.19085	10.2 "	0.50031
10.3 "	1.2025	10.3 "	0.505215
10.4 "	1.2142	10.4 "	0.51012
10.5 "	1.22587	10.5 "	0.515025
10.6 "	1.23755	10.6 "	0.519930
10.7 "	1.24922	10.7 "	0.524835
10.8 "	1.26090	10.8 "	0.529740
10.9 "	1.27257	10.9 "	0.534645
11.0 "	1.28428	11.0 "	0.539550

$\text{BaSO}_4 \times 0.137 = \text{Sulphur.}$

$\text{BaSO}_4 \times 0.34286 = \text{Factor} = \text{Sulphur trioxide.}$

$\text{BaSO}_4 \times 0.420 = \text{Factor} = \text{Sulphuric Acid.}$

To multiply factor with Barium Sulphate gives either S, SO_2 or H_2SO_4 .

The following is an addition to the interpolation table:

1.	2.	3.	4.
9.0 to 9.1	9.9 to 10.0	10.0 to 10.1	10.1 to 10.2
0.051917	1.156992	1.168667	1.180342
0.053084	1.158159	1.169834	1.1815092
0.054251	1.159326	1.171001	1.182676
0.055418	1.160493	1.172168	1.183843
0.056585	1.161660	1.173335	1.185010
0.057752	1.162827	1.17450	1.186177
0.058919	1.163994	1.175669	1.187344
0.060086	1.165161	1.176836	1.188511
0.061253	1.166328	1.178003	1.189678
0.06242	1.167495	1.17917	1.190845

Example: It has been found upon using 10 cc. of H_2SO_4 that 1.173335 BaSO_4 by weight, was obtained. Upon consulting table 3 this denotes that the solution of H_2SO_4 is 5/100 or 0.05 in 10 cc. too strong.

distilled water and boiled for a few minutes; to this solution is added a few cc. of conc. HCl or HNO_3 , stirred, and while boiling add the boiling or hot solution of barium chloride or nitrate 10 or 15 cc. (10 per cent solution); stir and mix, and keep mixed solution boiling for a further few minutes; then transfer to a warm place or water bath if convenient for settling of the macrocrystalline ppt. While the ppt. settles in water bath the porous crucible is heated and weighed which can be done very easily. I generally weigh the crucible under the same condition without the use of an exsiccator and was able to obtain very satisfactory results.

The weighed crucible is then attached to a water pump of any kind with the so-called carbon filter with rubber stopper, and a moderate stream of water will filter the hot barium sulphate ppt. absolutely clear through the porous clay crucible, leaving ppt. nearly white, and after washing with hot water, or better, slightly acidulated water to free the ppt. from barium chloride or nitrate which can be tested for such with silver nitrate or diphenylamin solution, in the filtrate. The porous crucible with ppt. is then carefully heated with a Bunsen burner and after moisture has been driven off the crucible can then be strongly heated and weighed to constancy.

I have worked out a table based on the principle of normal sulphuric acid 49.05 gm. of H_2SO_4 to 1,000 cc. distilled water figuring the acid from barium sulphate from 9 cc. to 11 cc. This will enable the chemist to know exactly the strength of acid to dilute or to make stronger if necessary. Ten cc., which averages to about 0.4905 gm. H_2SO_4 , is about or approximately the sufficient amount of any sulphate to be analyzed, with exception of sulphate ores, where there should be used in some cases 1 gm. and more.

This table can also be used for any sulphur analysis considering that the BaSO_4 as noted in the table corresponds to the product analyzed.

The crucible as such can be used for the analysis of different colloidal and semicolloidal ppts. with the same accuracy and less time. I have tried the crucible for different analyses and found it to be satisfactory.

A coalette factory has been established at Fort William, at the head of Lake Superior in Western Canada. Fort William was selected because here the great barge transportation companies have their wharves and coal dumps, and practically all the coal coming from Pennsylvania mines is routed through the Great Lakes to Fort William. This new \$100,000 enterprise is financed by Fort William capitalists, and has a contract with the railroad and lake transportation companies for coal dust or screenings collected on the dumps. The company has installed a Renfrew (plunger type) coalette machine, manufactured at St. Louis, Mo., with a capacity of 10 tons per hour. The method of manufacture employed does not differ materially from that in vogue in some parts of the United States, where the coal dust is briquetted with a hard pitch binder. The company has been quite successful, being able to market immediately its entire output, and is considering the installation of several new machines, and also operating night as well as day. It now employs over 25 men. The coalettes find ready sale in Canada as far west as Edmonton, and are sold in Winnipeg at \$9 per ton, as against \$10.50 for hard furnace coal. Wholesale prices vary from \$4.75 per ton f. o. b. for the coalettes made from American anthracite to \$5 per ton for those made from Pocahontas coal. The company does its business in the West through agencies.

ON THE PHARMACOPŒIAL ASSAY OF CITRAL IN LEMON OIL.*

By J. R. RIPPETOE, P. D., and LOUIS E. WISE, Ph.D.

The determination of Citral has for several years past been the subject of considerable investigation. In 1906 Chace¹ proposed a rapid method for the estimation of this aldehyde, which is applicable to the analysis of lemon oils and extracts and which time has shown to be admirably suited to the needs and requirements of the importer of the essential oils. Somewhat more recently Bennett,² modifying a method of Walther,³ has suggested a means of analysis depending on the use of hydroxylamine hydrochloride, and Romeo⁴ outlined a titration method which was published by the Messina Chamber of Commerce and successfully followed in the analysis of a number of pure oils.

In 1909 Hiltner⁵ published the description of a colorimetric method which together with that of Chace¹ has been outlined by Leach in his *Food Inspection and Analysis*.

The Pharmacopœial assay of oil of lemon is without doubt known to all pharmacists, chemists and analysts. In our hands, with careful manipulation and some degree of patience, it has given fair but not satisfactory results. We have found the end point very uncertain and we have always felt that the assay was extremely tedious, demanding much of the analyst's time and attention and frequently causing trouble and annoyance.

One of the chief sources of trouble is the sodium sulphite used in the analysis. During the course of some routine work we were much surprised to obtain results which could not be accounted for until we examined the reagent in question. Two analyses of the salt showed that it contained about 4 per cent of sodium sulphite instead of being chemically pure as the label stated. The rest had, with amazing rapidity, been oxidized to the sulphate. We studied this matter a little more closely and found that another sample of sulphite, containing water of crystallization, which had been assayed in June, and found to comply with the U. S. P. requirements, contained approximately 76 per cent of $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ in September. Elvove in a previous number of this journal⁶ has recorded a thorough investigation of this subject. Our only comment is that all sulphite should be roughly assayed by the U. S. P. method just before using and that an amount of salt should be taken, which contains the equivalent of 10 grams of anhydrous sodium sulphite or 20 gms. of sodium sulphite containing 7 molecules of water of crystallization for each 100 cubic centimeters of water used in making up the solution.

Another debatable point involves the amount of rosolic acid T. S. which is to be used in the assay. Our own experience has shown that the indicator should

be added at intervals during the course of the analysis until further addition causes no marked pink color in either the control or the test, after heating for a reasonable length of time in a water bath which is boiling briskly. We have found it best to add the rosolic acid solution from a calibrated 1 cc. pipette.

The end point is, as we have suggested, by no means sharp and brings a large personal error into play. After summing up the points of weakness of this assay, and adding to them the fact that Citronellal may be determined and reported as Citral, we reached the conclusion that, as a means of roughly approximating the true Citral content, the method was entirely too involved and laborious.

In trying to find a suitable substitute we have made some tests using the method outlined by Chace and also the one described by Hiltner.

Chace's fuchsin-sulphurous acid method was followed without great modification. (We found it convenient to use a refrigerator with a temperature of 13° to 13.5° C. and to make our comparisons at the end of 15 to 20 minutes.) For a description we refer the reader to Chace's original article or to Leach's *Food Inspection and Analysis*, page 866. Nessler tubes were used instead of a colorimeter, and varying amounts of a standard solution of pure Citral in aldehyde-free alcohol were employed for comparing color values. The method is rapid and gives results which are in general slightly higher than those given by the U. S. P. assay. Unfortunately this excellent and rapid method involves the use of aldehyde-free alcohol, a reagent which cannot be obtained in a short time. This handicaps the analyst who assays but few samples of the oil and who is called upon to report quickly. Under these circumstances he has little time to wait until the aldehyde has been removed. (We found that more than eight hours' boiling under reflux and that considerably more than 5 gms. of metaphenylene diamine hydrochloride were necessary to eliminate most of the aldehyde in 1,000 cc. of 95 per cent grain alcohol. Even then our distillates gave a distinct aldehyde reaction.)

Hiltner's method with slight changes has, however, proven sufficiently satisfactory to warrant a brief outline of the procedure followed in this laboratory. A more detailed description may be obtained from the author's original paper.

A standard solution of Citral made by weighing accurately between 50 and 70 mgms. of pure Citral and making up to 50 cc. with alcohol was found satisfactory. Each cubic centimeter then approximates 1 mgm. of Citral (100 to 130 mgms. in 50 cc. may be used and smaller aliquot portions taken for the test.)

Ninety-five per cent alcohol without previous purification was used in all the operations herein recorded. A 1 per cent solution of metaphenylene diamine hydrochloride in diluted alcohol was employed as reagent.

*From the American Journal of Pharmacy.

¹Journal of the American Chemical Society, 28, 1472.

²Analyst, 34, 1417.

³Pharm. Centr., 40, 621.

⁴Chem. Druggist, 74, 81.

⁵J. Ind. and Eng. Chem., 1, 798.

⁶American Journal of Pharmacy, 82, 211.

This solution was shaken with, and filtered through bone black before using.

About 1.5 cc. of oil of lemon is measured into a 50 cc. weighed flask, accurately weighed, and made up to the mark with 95 per cent alcohol, stoppered and thoroughly shaken. From two to four cc. of this solution are then accurately measured from a pipette calibrated to 1/100 cc. into a Nessler tube, 10 cc. of the filtered solution of metaphenylene diamine hydrochloride added, and the volume made up to the 25 cc. mark on the tube, with alcohol. The same or a corresponding amount of standard Citral solution is then pipetted into another tube and treated in the same way. The solutions after shaking are compared by viewing them transversely and the stronger one is diluted with 95 per cent alcohol until the reddish-yellow colors appear to be identical. The volumes are then measured and the subsequent calculations are based on the amount of Citral present in the standard. If these volumes vary more than 4 cc., one from the other, the test should be repeated using a relatively smaller amount of the stronger solution. We have found it advisable to compare the colors of the solutions when approximately 3 to 5 mgms. of Citral are present in the standard. Two or three close readings, all of them made in volumes of approximately 25 cc., should be obtained.

The method of calculating the results is comparatively simple. Taking as complex a case as possible:

Assume that each cc. of the standard contains 1.2 mg. of Citral, and that there are 1.30 grams of lemon oil in 50 cc. of an alcoholic solution. Then, if 3 cc. of the standard and 3.2 cc. of the solution of oil of lemon are used in the test—and if the *final* volume of the standard is 26 cc. (after colorimetric comparison and dilution) and provided the other solution measures 25 cc.—

Each cc. of the *diluted standard* is equivalent to $\frac{1.2 \times 3}{26}$ each cc. of the *other solution*, and contains _____ mgms. of Citral.

The *total final* volume of the unknown (oil of lemon) solution then contains $\left[\frac{1.2 \times 3}{26} \right] \times 25$ of 3.46 mgms. of Citral.

In other words 3.2 cc. of the original solution of oil of lemon contain 3.46 mgms. of Citral and 3.2 cc. of *this same solution* also contains 83.2 mgm. of oil

$$\left(\frac{1.300}{50} \times \frac{3.2}{1} \times \frac{100}{1} = 83.2 \right).$$

3.46 mgm. Citral
Then $\frac{\text{3.46 mgm. Citral}}{\text{83.2 mgm. of oil}} \times 100 = \text{Percentage Citral in the oil} = 4.16 \text{ per cent.}$

It may be of interest to note the close readings which can be obtained by the metaphenylene diamine method. They are shown in Table I.

TABLE I.

Sample number.	Per cent citral (Hiltner's method).
IIa	3.88; 3.89
IIb	4.19; 4.22; 4.07
9469	4.05; 3.89
9427	4.11; 4.11

Table II shows the Citral content of the oils as determined by the three methods.

TABLE II.

Sample number.	By U. S. P. method. Per cent.	By Chace's method. Per cent.	By Hiltner's method. Per cent.
II	4.17		4.16
	4.44	4.20	3.89
9469	4.30	4.50	3.97
9427	4.04	4.35	4.11

As a result of this limited investigation, we beg to recommend that the Hiltner method be further studied, and that if possible, it be substituted for the pharmacopœial sulphite method now in use. The former is apparently more accurate (since it does not determine the Citronellal and thus introduce a positive error) and is undoubtedly much more rapid and far less troublesome. The results obtained may naturally be somewhat lower and if the method is adopted it may be found necessary to change the U. S. P. requirements from 4 per cent to approximately 3.8 per cent of Citral.

Among the manufacturers of Moscow, Russia, a company is being organized to build a new factory for the manufacture of artificial silk and other products made from cellulose. The purpose is to supply the home trade as well as to export. The company is now acquiring a large estate in Bogorodsk County, Moscow Province, in which there are several large factory buildings.

The gold-mining industry was generally active in 1911, but early figures indicate a total production for the United States and Alaska slightly below the output of 1910. The most notable features of the industry in 1911, according to H. D. McCaskey, of the United States Geological Survey, were the resumption of normal labor conditions in the Black Hills of South Dakota, the increased dredge output in California, development of production in the new Innoko-Iditarod placer region of Alaska and the Republic district of Washington, continued development and prosperity of the great Goldfield (Nevada) and Treadwell (Alaska) mines, normal conditions also on the Mother Lode in California, improvement in metallurgical methods, and general increase in activity at many small deep and placer mines. Renewed interest in prospecting was shown in Colorado, although the gold output of the State decreased owing to the gradual exhaustion of several large ore bodies and to continued small decrease in production from the great Cripple Creek camp. Preliminary figures of the Director of the Mint indicate a total domestic gold output of \$96,233,528 in 1911, against \$96,269,100 in 1910.

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THE WASHINGTON MEETING OF THE AMERICAN CHEMICAL SOCIETY.

Again the American Chemical Society has held the largest meeting in its history, 658 members and guests registering in Washington, and probably 700 were present.

The meeting opened on Wednesday, December 27th, with a joint meeting of the Section on Chemical Education and the Division of Physical and Inorganic Chemistry, at which the following four papers were given:

A. A. Noyes, Chairman, "The Teaching of Physical Chemistry."

W. D. Bancroft, "Physical Chemistry in the Introductory Course."

H. C. Jones, "The Introduction of Physical Chemical Conceptions in the Early Stages of the Teaching of General Chemistry."

J. Howard Mathews, "Some Applications of Color Photography in the Teaching of Physical Chemistry." (Illustrated.)

In the afternoon the address of Vice-President

Frankforter, of Section C, entitled "The Resins and Their Chemical Relations to the Terpenes," was delivered before a large audience and was followed by an address by Chairman H. P. Talbot on the subject "Privileges and Responsibilities of the Chemical Analyst." Following Dr. Talbot, Dr. A. L. Voge, of the Library of Congress, read a paper on "Ostwald's Proposed International Institute of Chemistry."

Throughout the week the Society's Divisions of Agricultural and Food Chemistry, Biological Chemistry, Industrial Chemists and Chemical Engineers, Fertilizer Chemistry, Organic Chemistry, Pharmaceutical Chemistry, Physical and Inorganic Chemistry, and the Chemistry of India Rubber, held meetings in rooms especially assigned to them.

Some 500 were present at the "smoker" on Wednesday evening, which was fully up to the standard of the well-known smokers of the Chemical Society.

On Thursday evening Alexander Smith, president of the society, delivered his presidential address, entitled "An Early Physical Chemist," and was followed by an interesting lecture by Frank B. Kenrick and H. E. Howe, consisting chiefly of illustrations by means of the lantern of the effect of temperature, pressure, concentration, surface tension, osmotic pressure, etc., on reactions in heterogeneous systems.

A feature of the divisional meetings was the Symposium on Mineral Wastes and Their Conservation, held before the Division of Industrial Chemists and Chemical Engineers on Friday. The following papers were presented and the discussion was prolonged throughout the day:

J. A. Holmes, "Carbon Waste."

W. H. Bassett, (a) "Zinc Losses in Brass Manufacture," (b) "Need of Special Alloys for Special Uses."

W. R. Whitney, "New Uses to Reduce Abuses in Conservation."

A. V. Bleining, "Wastes in the Ceramic Industry."

A. D. Little, "The Abuse of Brand."

F. K. Cameron, "Waste and Conservation of Potash and Phosphoric Acid."

F. G. Cottrell, "Sulfur Fumes and Flue Dust."

Charles L. Parsons, "Miscellaneous Mineral Wastes."

The Division of Pharmaceutical Chemistry held a Symposium on Drug Assaying on Friday morning, and on Friday afternoon a joint meeting of the Society of Biological Chemists was held with the biological chemists of the American Chemical Society.

The secretary's report showed an increase of members of over five hundred for the year, the society's membership standing on December 1st at 5,603. During the year the society spent over \$55,000 on its journals, returning to each paid member in actual cost of publications more than 100 per cent of his dues.

At the meeting of the Council on Tuesday afternoon and evening the Biological Section of the society was authorized to form a Biochemical Division, elect-

ing its own officers, and two new local sections were formed—one at Detroit and one at New Haven.

Interesting reports were received from the Committee on Standard Methods of Analysis and from the Committee on Patent and Related Legislation.

It was voted to donate the library of the American Chemical Society to the New York Chemists' Club on condition that members of the society have ready access thereto.

The question of the time of the annual meetings of the society was vigorously discussed, many members favoring a change from the winter season to Easter week, and a committee was appointed to take this into consideration and report to the Council.

The election of the following officers was announced for 1912: A. D. Little, President; C. L. Parsons, Secretary; A. P. Hallock, Treasurer; W. A. Noyes, Editor of the Journal of the American Chemical Society; A. M. Patterson, Editor of Chemical Abstracts; M. C. Whitaker, Editor of the Journal of Industrial and Engineering Chemistry; E. G. Love and Alexander Smith, Directors for two years; S. W. Parr, W. H. Walker, W. L. Miller and W. D. Bigelow, Councilors at Large for three years; C. H. Herty, Councillor at Large to fill the unexpired term of A. D. Little; E. G. Love, G. C. Stone and A. E. Hill, Finance Committee; Wm. McMurtrie, C. L. Parsons and B. E. Curry, Membership Committee.

Over 250 papers were presented at the meeting.

According to the Mining and Scientific Press phosphates containing 35 per cent of P_2O_5 are produced in Sweden by a recently devised process. During the exploitation of the Gellivara mines, enormous quantities of ore too poor in apatite to be utilized were left. Now that the immense electric power-house supplied by the Porgus waterfalls has been constructed, it is proposed to work these heaps of debris. The poor ores are first sorted mechanically, and then treated by the process devised by W. Palmer, of the Stockholm University. The diphosphate of calcium can be obtained by subjecting the apatite to the action of hydrochloric acid produced by the electrolysis of common salt. The salt is regenerated, and can be again used. For 1 kw.-hp., 3 tons of the diphosphate of calcium can be produced annually from 11 tons of the residue containing apatite. It is estimated that Gellivara will be capable of supplying 11,000 tons of phosphate per year, for which 5,000 to 6,500 H. P. will be necessary. There are also similar large waste heaps at Kirunawara, Svapparara, and Ekstroberg, equally amenable to electric treatment.

C. L. PARKER

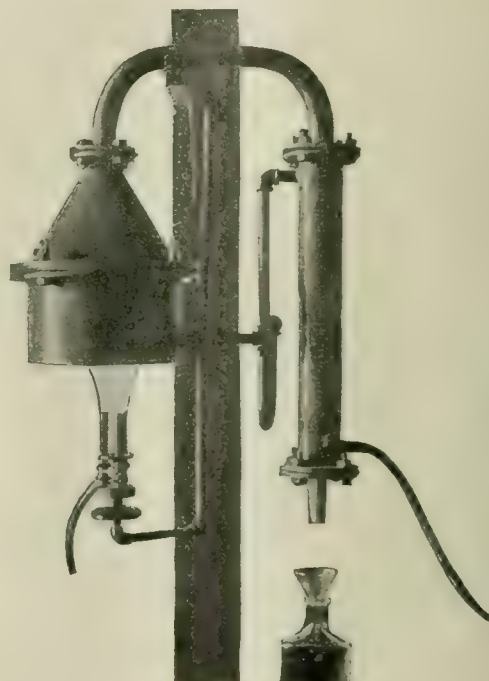
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No. 2.

AN INVESTIGATION OF THE STRENGTH OF ROLLED ZINC.

Zinc is used as a constituent of brass and other alloys, as a protective coating for iron and steel plate and pipe, and as a preventive against rusting out of steam boiler tubes. It is used for making fruit jar covers and corrosion-resisting cans and boxes. In the form of wire, it is used for making shoe nails, and in the form of plates, it is used for making etchings (line cuts) for the reproduction of drawings. Zinc has a wide use as the electro-negative element in electric batteries. The ductility of zinc is an important factor in the manufacture of fruit jar covers, cans, battery zincs, or in other cases when it is to be bent or stamped into shape. Zinc is rarely used as a stress-carrying member of a machine or structure; in Europe thin zinc plates are sometimes used for roofing, and in a few cases electric cables have been suspended by strips of sheet zinc, which resist atmospheric corrosion better than do strips of steel plate.

The occasional use of sheet zinc hangers for supporting electric cables called the attention of the Matthiessen & Hegeler Zinc Co. of La Salle, Ill., to the question of the strength of rolled sheet zinc, and it was found that few data were available. The matter was referred to the attention of the Engineering Experiment Station of the University of Illinois, and the general subject of the strength of rolled zinc seemed to be of sufficient importance to warrant making tests. A series of tests of strength of zinc was made in the Laboratory of Applied Mechanics of the University of Illinois, by Herbert F. Moore, Assistant Professor in Theoretical and Applied Mechanics, under the general direction of Professor Arthur N. Talbot, head of the Department of Theoretical and Applied Mechanics. The results of this investigation are described by Prof. Moore in a bulletin issued recently by the University of Illinois. From this bulletin we have abstracted the matter in this article.

In addition to tension tests of zinc, tests of rolled zinc under punching and shearing were made. In the course of the investigation, several tests of cast zinc were made, including torsion and compression tests, and also cold bending tests of rolled zinc.

EXISTING DATA ON STRENGTH OF ROLLED ZINC.

The principal tests on the strength of rolled zinc

have been made by Bauschinger, Martens and Meyer. Bauschinger's tests¹ showed the effect of rapidity of loading on the properties of zinc. The influence of duration of test on the strength of cast zinc was slight, but with rolled zinc, rapidity of testing increased the tensile strength. In tests lasting 6 min., the average ultimate tensile strength was 29,100 lbs. per sq. in.; in tests lasting 81 min., the average ultimate tensile strength was 23,300 lbs. per sq. in.

TABLE I.—TENSION TESTS OF ROLLED ZINC; EFFECT OF THICKNESS AND OF DIRECTION OF ROLLING (MARTENS).

Thickness of plate— inches.	Ultimate Tensile Strength lb. per sq. in.	
	With grain (parallel to direction of rolling).	Across grain (perpendicular to direction of rolling).
0.019—0.222	26,600—14,200	31,800—20,200

TABLE II.—TENSION TESTS OF ROLLED ZINC; EFFECT OF TEMPERATURE OF TEST SPECIMEN (MARTENS).

Temperature of specimen degrees Fahr.	Ultimate tensile strength lb. per sq. in.	Elongation after rupture per cent.
66—81	20,600	12.4
176	12,500	29.4
248	8,960	59.4
302	5,790	101.5
338	7,960	17.1
392	6,120	7.2

Martens² investigations of the strength of zinc dealt with the influence on strength of thickness of plate, of direction of rolling and of temperature. His results are summarized in Table I and Table II. From these results, it would seem that about 300° F. is the most favorable rolling temperature for zinc plates, as at that temperature the strength is low and the ductility a maximum. All Martens' tests were made on zinc refined from Silesian ores.

An extensive series of tests of the strength of zinc plates was made by Dr. Oswald Meyer of Vienna.³ The plates tested by him were all rolled at the zinc works of Cilli, in Austria. The plates contained from 0.021 to 1.04 per cent of lead, 0.03 to 0.912 per cent of cadmium, 0.02 to 0.03 per cent of iron, from a trace to 0.009 per cent of copper, and a trace of arsenic. Tests were made of (a) plates as received from the zinc works; (b) plates treated with nitric acid; and (c) plates subjected to heat treatment before testing. The results of Meyer's tension tests of plates as received from the zinc works, are shown in Table III.

¹Mitteilungen aus dem mechanisches—technische Lab. der Technische Hochschule im Munchen, 1887, Heft 20, Seite 16.
²Mitteilungen aus mech.—tech. Versuchsanstalten in Berlin, Ergänzungsheft IV.

The following features of Meyer's tests are worthy of note. Specimens cut across grain (perpendicular to the direction of rolling) are somewhat stronger and stiffer than specimens cut with the grain (parallel to the direction of rolling).

The ductility of specimens cut with the grain is greater than that of specimens cut across the grain. Stresses at elastic limit and yield point are very low, the yield point is not sharply marked, and the flow of metal under high stress goes on for a long time.

TABLE III.—TENSION TESTS OF ROLLED ZINC (MEYER).

Tests of zinc as received from the rolling mill.			
Thickness of plate tested varied from 0.044 in. to 0.051 in..			
Item.	With grain.	Across grain.	Average.
Stress at first permanent set, per sq. in.....	1,990	2,420	2,130
Stress at limit of proportionality of stress to deformation, lb. per sq. in.....	710	1,280	995
Yield point, lb. per sq. in.	11,400	13,640	12,500
Ultimate, lb. per sq. in...	30,400	36,800	33,600
Elongation, per cent....	27.2	9.7	18.5
Reduction of area, per cent	43	17	30
Modulus of elasticity, lb. per sq. in.....	12,850,000	14,500,000	13,620,000

The tests of zinc plates treated with acid show that a 10 min. immersion in 5 per cent nitric acid did not appreciably lessen the strength or the ductility of the zinc plate.

A series of tests was made by Dr. Meyer on zinc plates subjected to the following heat treatment before testing in tension: The specimens were subjected for one hour to a temperature of 527° F., when upon testing they developed the properties indicated in Table IV. (average values).

The ultimate strength in tension and the ductility are decidedly lowered by this heat treatment. The "critical temperature" for zinc was found to be at about 300° F. and the heat transformation of the zinc took place very rapidly, one minute being seemingly sufficient to effect it. The tests of Martens and of Meyer point to the desirability of keeping the working temperature during the rolling of zinc within narrow limits. Meyer recommends 302° F. as a maximum rolling temperature.

Meyer also made tests to show the effect of alloying zinc with cadmium and with lead. He found that the addition of 0.2 per cent of cadmium improved the quality of zinc plate, but that the addition of 0.4 per cent of either cadmium or lead either produced no appreciable effect or injured the quality. The addition of both cadmium and lead lowered both the strength and the ductility of zinc plate.

The Matthiessen & Hegeler Zinc Co. of La Salle, Ill., report a series of tension tests of zinc plate made at their request in 1907. The thickness of the plate tested varied from 0.011 in. to 0.04 in., the average tensile strength for sixty specimens was 29,370 lbs. per sq. in. The thinner plate showed slightly greater strength than the thicker plate.

Source of Supply of Zinc for Tests.—The zinc tested at the University of Illinois came from the zinc works of the Matthiessen & Hegeler Zinc Co. at La Salle, Ill., and from the stock of a local hardware store. The zinc from the Matthiessen & Hegeler Co. was smelted from ores from the Joplin, Mo. district. Several specimens of cast zinc were furnished which were refined in spelter poured directly into moulds.

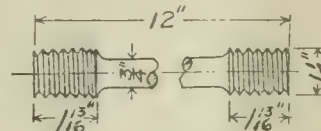


Fig. 1.

Eighteen sheets of rolled zinc, each 18 in. by 20 in., were furnished, varying in thickness from 0.006 in. to 1.0 in. Three sheets of each thickness were furnished, and each of the three sheets was from a different heat. No special precautions as to heat treatment were taken either with the cast zinc or with the rolled zinc. As a check on the values obtained for the zinc plates furnished by the Matthiessen & Hegeler Zinc Co., tests were made on sheet zinc purchased in the local market (Champaign, Ill.).

Test Specimens.—Specimens of cast zinc were tested in tension in compression, and in torsion. Specimens of rolled zinc were tested in tension, in cold bending and in shear; the tests in shear included punching tests and tests in direct shearing. The specimens for tension tests of cast zinc were similar in form and dimension to the specimen shown in Fig. 1. The cast zinc was furnished in bars 1 1/4 in. square by 12 ins. long and machined to the size shown in Fig. 1.

The plates of rolled sheet zinc furnished by the Matthiessen & Hegeler Co. were 18 ins. by 20 ins. in size. The specimens similarly located in different plates were stamped with the same number, the plate

TABLE IV.—TENSION TESTS OF HEAT TREATED ZINC (MEYER).	
Stress at first permanent set.....	2,480 lb. per sq. in.
Stress at limit of proportionality of stress to deformation.....	1,710 lb. per sq. in.
Yield point.....	11,100 lb. per sq. in.
Ultimate	17,500 lb. per sq. in.
Elongation	4.6 per cent
Reduction of area.....	5 per cent
Modulus of elasticity.....	15,950,000 lb. per sq. in.

being designated by a letter. The strips from which the specimens for tension tests of rolled zinc were machined out were sheared from an 18 in. by 20 in. plate in all cases except some of the plates 1.0 in. thick,

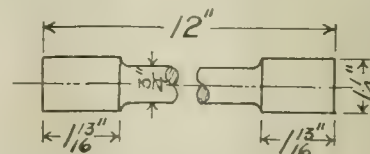


Fig. 2.

in which it was found impossible to shear strips from the plate without seriously injuring it. In these thick plates, the strips from which the tension specimens were machined were cut from the plates by drilling. The tension specimens of rolled zinc were machined on a shaper.

The punching and shearing tests for rolled zinc

were made on the portion of the 18 in. by 20 in. plates remaining after the tension test pieces had been cut out. The holes punched in the punching tests were separated by a distance at least $1\frac{1}{2}$ times the diameter of the punch used. The shearing tests were made on specimens cut from the portion of the plates left after the punching tests had been made. The shearing test specimens were cut 1 in. wide, and were sheared in double shear. Some specimens were sheared across the grain (perpendicular to the direction of rolling) and some with the grain (parallel to the direction of rolling).

Cold bending tests were made on small strips of zinc about 1 in. wide cut from any portion of the 18

results of tension tests shows that zinc, either cast or rolled, is imperfectly elastic under very low stresses. The results of Meyer's tests are in agreement with the results of the Illinois tests as regards this general conclusion, though in the Illinois tests permanent set was detected at lower stresses than in Meyer's tests. Whether the elastic limit be defined as the lowest stress under which a material is given a permanent set, or as the lowest stress at which Hooke's law (proportionality of stress to deformation) is found to be inexact, the elastic limit of zinc is very low and very poorly defined. It is doubtful if the elastic limit as determined either by Meyer or in the Illinois tests has any special physical significance. Though Meyer

TABLE V.—TENSION TESTS OF ZINC.

Thickness of rolled plate in.	Number of specimens.	Stress at first noticeable. Set lb. per sq. in.	Stress limit of proportionality lb. per sq. in.	Stress at ultimate lb. per sq. in.	Modulus of elasticity lb. per sq. in.	Elongation in 8-in. per cent.	Reduction of area, per cent.	Speed of pulling in. per min.	Specimens tested with or across grain.
Cast	6	1,600	2,100	9,060	11,025,000	slight	slight	hand	
1	5	0+*	0+	22,200		7.56	8.72	0.3	With grain.
1	4	900	2,900	21,340	10,450,000	4.85	6.58	0.5	With grain.
1	3	900	4,600	23,050	10,370,000	0.31	5.37	0.5	Across grain.
0.6	12	0+	4,200	21,490	11,033,000	16.63	22.25	0.5	With grain.
0.6	5	0+	4,000	23,550	10,780,000	3.33	5.80	0.5	Across grain.
0.25	12	0+	5,150	23,770	12,767,000	11.90	19.17	0.5	With grain.
0.25	6	0+	5,000	22,260	10,967,000	0.27	5.07	0.5	Across grain.
0.10	6	0+	3,600	22,280	10,650,000	18.75		0.5	With grain.
0.10	6			24,870		21.00		3.25	With grain.
0.10	6	0+	5,500	33,620	13,700,000	14.3		0.5	Across grain.
0.018	6	0+	5,800	25,490	10,533,000			0.5	With grain.
0.018	2			29,810				1.37	Across grain.
0.018	3			23,840				0.2	With grain.
0.018	6			34,960				0.5	Across grain.
0.006	6			24,110				0.2	With grain.
0.006	6	0+	5,100	26,480	14,800,000	6.5		0.5	With grain.
0.006	3			33,830				0.5	Across grain.
0.006	3			38,440				2.5	Across grain.
0.018†	3			24,200				0.5	With grain.
0.018†	2			35,150				0.5	Across grain.

*When a stress is given as 0+, a value below the lowest reading taken is denoted.

†Specimens from zinc bought in the local market; all specimens not specially designated were cut from zinc furnished by the Matthiessen & Hegeler Zinc Company.

in. by 20 in. plates remaining after the other tests had been made. For each plate tested in cold bending, one specimen was bent in a plane parallel to the direction of rolling (with the grain), and one specimen was bent in a plane perpendicular to the direction of rolling (across the grain).

The sheet of zinc bought in the local market differed in size from those furnished by the Matthiessen & Hegeler Co., but the general method of cutting specimens from it was the same as that just described.

Table V shows the summarized results of tension tests of zinc. In this the values given are the average results for the number of specimens noted in the second column of the table. Table VI shows the results of the punching tests, and Table VII shows the results of the shearing tests. In both of these the values given are the average results for the numbers of specimens noted in the second column of the tables.

RESULTS AND CONCLUSIONS.

Tensile Strength of Zinc.—An examination of the

reported a yield point of zinc in the tables of results of his tests, in the accompanying discussion he stated that the yield point was poorly defined. In the Illinois tests no well-defined yield point could be detected, and none was reported.

The ultimate tensile strength of cast zinc depends on the temperature of pouring, and other factors, and varies between wide limits. Thin plates of rolled zinc are relatively stronger under tension than thick plates. From the results of the Illinois tests for plates under 0.05 in. thick, 24,000 lbs. per sq. in. would seem to be about the value to be used for the ultimate tensile strength of rolled zinc. For plates over 0.05 in. thick, 21,000 lb. per sq. in. would seem a reasonable value to use. Meyer's tests and those of the Matthiessen & Hegeler Zinc Co. show slightly higher values. Rolled zinc is somewhat stronger in tension across the grain than in tension with the grain. A higher tensile strength of rolled zinc was obtained by increasing the rapidity of application of load. Rapidity of testing

may, in part, account for the fact that higher values of tensile strength were found by Meyer and by Matthiessen & Hegeler than were found at Illinois. Neith-

TABLE VI.—PUNCHING TESTS OF ZINC.

Nominal thickness of plate, ins.	Number of specimens tested.	Diameter of punch, ins.	Speed of punching, ins. per min.	Ultimate shearing stress developed, lbs. per sq. in.	Energy required to punch in. lb. per sq. in. per in. thickness.
1.00	6	0.75	0.10	18,750	7,260
1.00	6	1.00	0.10	19,060	6,650
0.60	6	0.50	0.10	19,740	10,590
0.60	6	0.75	0.10	19,350	8,630
0.60	6	1.00	0.10	18,990	6,400
0.25	6	0.50	0.10	20,000	10,550
0.25	6	0.75	0.10	19,700	8,740
0.25	6	1.00	0.10	19,390	8,030
0.25	6	1.00	0.50	19,400	8,350
0.25	6	1.00	1.60	20,850	8,380
0.10	6	1.00	0.10	18,230	5,650
Av.				19,400	8,110
0.018*	9	1.00	0.10	12,930	
0.018*	6	1.00	0.10	13,380†	
0.018*	9	1.00	0.10	10,880	

*In the very thin plates, shearing took place unevenly around the circumference of the punching tool.

†Zinc bought in the local market.

er of the first two reports the speed of testing. The speed used in the Illinois tests was lower than is sometimes used in commercial testing.

From the results of the various tension tests of zinc herein quoted, it would seem that the modulus of elasticity of zinc is about 11,500,000 lbs. per sq. in.

Shearing Strength of Rolled Zinc.—The values of shearing strength of rolled zinc were determined with the purpose of throwing some light on the problem of what sizes of punches and shears should be used in working with zinc plates. Two factors which are important in their influence on the design of punches and shears are the maximum force to be exerted during the process of punching or shearing and the energy required to complete the punching or shearing action. The maximum force to be exerted determines the strength of frame, ram, gearing, and other parts of the punch or shear, the energy required determines, in large measure, the weight of the flywheel, size of belt, and power required for power-driven punches and shears, or the power and amount of water or air required for hydraulic or pneumatic punches or shears. The maximum force to be exerted during the punching or shearing action is in general proportional to the area actually sheared under the action of punching or shearing tool; the mean force during the action is approximately proportional to the maximum force and consequently to the area under the action of the punching or shearing tool. The energy required to punch or shear any plate will then be approximately proportional to the area to be sheared (by punching or shearing tool) multiplied by the distance traveled by the tool during the punching or shearing action, i. e., by the thickness of the plate. The significant features of

the punching or shearing tests of rolled zinc were, then, the maximum shearing stress developed measured in pounds per square inch, and the energy required for punching or shearing measured in inch-pounds per square inch of surface sheared per inch thickness. An examination of the results of the punching and shearing tests of zinc plate shows an average value of shearing stress developed of 19,400 lbs. per sq. in. for the punching tests, and of 17,100 lbs. per sq. in. for the shearing tests. The average value of the energy required was 8,110 in. lb. per sq. in. per in. thickness for the punching tests, and 4,850 in. lb. per sq. in. per in. thickness for the shearing tests. Evidently the frictional resistance of the metal pushed out (the "wad") is greater in punching than in shearing, as is shown by the slightly greater stress developed, and by the markedly greater energy required.

An examination of the results of the punching tests shows that the larger the punch for any given thickness of plate the less the unit-energy required to punch the plate. In both punching and shearing tests, the maximum stress developed was slightly increased under increased speed of punching or shearing tool.

Both punching and shearing tests were made with flat-faced tools, the object being to bring stress as uniformly as possible on all parts of the area under shear. By the use of beveled punching and shearing tools, the maximum force resisting shear would have been reduced.

An examination of the results of the punching and

TABLE VII.—SHEARING TESTS OF ZINC.

Nominal thickness of plate, ins.	Number of specimens tested.	Speed of shearing tool, ins. per min.	Ultimate shearing stress developed, lbs. per sq. in.	Energy required to shear in. lb. per sq. in. per in. thickness.	Shearing with grain or across grain.
1.00	6	0.10	16,700	4,850	Across grain.
1.00	3	0.10	16,580	4,510	With grain.
1.00	6	0.50	17,140	4,130	Across grain.
1.00	6	1.60	17,770	4,330	Across grain.
0.60	6	0.10	16,580	5,100	Across grain.
0.60	3	0.10	17,380	4,620	With grain.
0.60	6	0.50	15,480	4,640	Across grain.
0.60	6	1.60	18,100	4,410	Across grain.
0.25	6	0.10	18,860	6,690	Across grain.
0.25	3	0.10	18,170	4,620	With grain.
0.25	6	0.50	15,480	4,640	Across grain.
0.25	6	1.60	17,040	5,730	Across grain.
Av.			17,100	4,850	

shearing tests of mild steel plate (see Tables VIII and IX) tested for purposes of comparison with rolled zinc shows the following average values: Shearing stress developed, 50,450 lbs. per sq. in. for the punching tests, 43,270 lbs. per sq. in. for the shearing tests. Energy required 25,200 in. lb. per sq. in. per in. thickness for the punching tests, and 16,910 in. lb. per sq. in. per in. thickness for the shearing tests.⁴ In punching or shearing zinc plates, about 40 per cent as high a stress is developed as is developed in punching or

shearing mild steel plates of the same size, and about 30 per cent as much energy is required.

Ductility and Plasticity of Zinc.—For the comparison of the ductility of different metals there is, unfortunately, no well defined quantitative standard. In the

TABLE VIII.—PUNCHING TESTS OF STEEL PLATE.

Nominal thickness of plate, ins.	Number of specimens tested.	Diameter of punch, ins.	Speed of punching, ins. per min.	Ultimate shearing stress developed, lbs. per sq. in.	Energy required to punch in. lb. per sq. in. per in. thickness.
0.375	2	0.75	0.10	50,000	30,350
0.375	2	1.00	0.10	50,080	19,880
Av. 50,040				25,200	

series of tests described in this bulletin the elongation and the reduction of area after rupture in tension and the results of cold bending tests were all used to throw light on the ductility of the zinc tested. From the results of the tests, it is evident that zinc is much

TABLE IX.—SHEARING TESTS OF STEEL PLATE.

Nominal thickness of plate, ins.	Number of specimens tested.	Speed of shearing tool, ins. per min.	Ultimate shearing stress developed, lbs. per sq. in.	Energy required to shear in. lb. per sq. in. per in. thickness.	Shearing with grain or across grain.
1.000	2	0.10	44,700	11,580	Across grain.
0.625	2	0.10	37,200	17,750	Across grain.
0.375	3	0.10	46,970	18,850	Across grain.
0.375	3	0.50	43,000	16,740	Across grain.
0.375	2	1.60	44,500	19,630	Across grain.
Av. 43,270			16,910		

less ductile than wrought-iron or mild steel, and that it is less ductile across the grain than with the grain. For zinc plate which is to be stamped or bent into shape (for example in the making of zinc elements for dry batteries), a severe cold-bending test would

TABLE X.—TORSION TESTS OF CAST ZINC.

Number of specimens tested.....	6
Maximum fiber stress at limit of proportionality of stress to angle of twist	5,450 lbs. per sq. in.
Computed maximum fiber stress at rupture	15,260 lbs. per sq. in.
Modulus of elasticity in shear (Torsion)	4,570,000 lbs. per sq. in.

TABLE XI.—COMPRESSION TESTS OF CAST ZINC.

Number of specimens tested.....	4
Fiber stress at limit of proportionality of stress to compression.....	1,620 lbs. per sq. in.
Modulus of elasticity.....	6,900,000 lbs. per sq. in.

seem to be of considerable value in determining the acceptability of a shipment of zinc plate.

The researches of Martens and of Meyer on the

effect of heat treatment of zinc on its strength and ductility would indicate the desirability of measuring and of controlling the temperature in the rolling process and show the danger of rolling at too high a temperature. While the ductility of zinc is low as compared with that of steel, from the low and poorly defined elastic limit, from the loss of energy in "mechanical hysteresis" and from the behavior of compression test pieces it is evident that the zinc possesses a relatively high degree of plasticity.

Summary—The following summary is given:

1. Zinc either rolled or cast has no well-defined

TABLE XII.—COLD BENDING TESTS OF ROLLED ZINC.

Nominal thickness of plate, ins.	Specimen bent with grain or across grain.	Action under Cold Bending.
0.006	Across grain	Bent double and hammered flat without cracking.
0.006	With grain	Bent double and hammered flat without cracking.
0.018	Across grain	Bent double and hammered flat without cracking.
0.018	With grain	Bent double and hammered flat without cracking.
0.018*	Across grain	Bent double and hammered flat without cracking.
0.018*	With grain	Bent double and hammered flat without cracking.
0.100	Across grain	Two specimens bent double and hammered flat without cracking; one specimen cracked when hammered flat.
0.100	With grain	All specimens bent double and hammered flat without cracking.
0.250	Across grain	Specimens cracked when bent through 90-120 degrees.
0.250	With grain	One specimen bent double and hammered flat without cracking; two specimens cracked after bending through 180 degrees.
0.600	Across grain	One specimen tested, broke short off when bent through about 30 degrees.
0.600	With grain	One specimen tested, cracked after bending through 180 degrees.

yield point and its elastic limit is very low. Zinc possesses a relatively high degree of plasticity.

2. The ultimate tensile strength of thin rolled zinc plate (not more than 0.05 in. thick) is about 24,000 lb. per sq. in.

3. The modulus of elasticity of zinc in tension is about 11,500,000 lb. per sq. in.

4. The stress per square inch of area sheared developed in punching or shearing rolled zinc plates is about 40 per cent of the stress developed in punching or shearing mild steel plates.

5. The energy per square inch of area sheared per inch thickness of plate required to punch or shear rolled zinc plates is about 30 per cent of the energy required to punch or shear mild steel plates.

6. The ductility of rolled zinc is much less than that of mild steel, and the ductility of zinc plate with the grain is greater than the ductility across the grain.

*Other punching and shearing tests of mild steel give results not widely differing from these. See article by H. V. Loss in the American Engineer and Railroad Journal for March 1893 and results in Kent's Mechanical Engineers' Pocket Book.

WHAT MAKES WHITE LEAD CHALK AND HOW CHALKING MAY BE PREVENTED.*

By HENRY A. GARDNER.†

The chalking of white lead is one of the evils attending the use of this valuable white paint pigment which the master painter is most anxious to correct. Every fair observer will probably admit that moderate chalking is not objectionable, as it leaves a surface for repainting which will quickly receive and amalgamate with the new paint applied; this result being difficult with an old painted surface which is excessively hard or brittle. Excessive chalking, however, which is often followed by deep alligatoring and gradual disintegration, should be avoided if possible, for no matter how good a paint may be placed over a deeply-checked surface, the result is always unsatisfactory and unsightly.

The writer has recently read with interest a pamphlet which attempts to explain the cause of the chalking that is exhibited by nearly all pure white lead paints after exposure to the elements. In the article referred to, some very interesting theories have been advanced, and the object of this paper is to briefly outline these theories and discuss them in the light of the most recent knowledge obtainable on the subject.

It has been stated in the pamphlet referred to that the chalking of white lead is due to the lack of linseed oil, and that chalking would not take place to any extent if white lead paints were mixed with greater quantities of linseed oil. From an economical standpoint, it would appear to the writer that if painters were to follow the above suggestion and use greater quantities of linseed oil than is at present the prevailing practice the effect would not be towards relief from the present high prices which must be paid for pure oil, and might not only encourage the use of linseed oil substitutes which have not been thoroughly tested, but actually lead to the use of such substitutes.

It has further been stated that not only the priming coat of white lead but the top coat as well should receive very long oil reductions in order to form a film which would protect the pigment from the elements, which are the initial cause of chalking when lead is applied with the usual short oil reduction. The application of ordinary white lead paint has been compared with the application of short oil varnishes which contain quantities of gum with very little oil, the analogy suggesting that the same enduring results which are obtained on exposure of long oil varnishes would be obtained if lead paints were reduced with quantities of oil. Commenting on the above procedure, it would appear to the writer that the use of larger quantities of oil than are at present in com-

mon use would result in a paint deficient in hiding power and strength. Furthermore, the comparison of varnishes with paints is not justified, as a varnish which consists of gums dissolved in oil is an entirely different material from an oil in which pigments are simply suspended. Both of these materials must be studied along separate lines, as they are physically and chemically different.

It is well known that linseed oil, or, in fact, any oil, when spread into a paint film to a coating which upon exposure does not possess any very great strength or moisture-excluding power. When linseed oil, however, has been ground with pigments, the strength of the films is increased materially, and the greatest strength is developed in those cases in which a critical percentage of pigment has been added to the oil. The critical percentage varies with the nature of the pigment, a small quantity of some pigments being sufficient, while a large quantity of other pigments is necessary, to produce films of maximum strength. An average paint consists of ten pounds of pigment suspended in one gallon of oil, but the writer has in mind at present a paint made from 35 lbs. of pigment suspended in 1 gal. of oil. This pigment, namely, American vermilion (basic chromate of lead), is probably the lowest oil-carrying pigment ever produced or applied under actual practical conditions, and to-day, after nearly four years' exposure along the Atlantic coast, where it has been subjected to the most severe atmospheric conditions, it is in almost perfect condition, showing absolutely no chalking. Being a lead pigment and being applied with a shorter oil reduction than white lead has ever been applied with, the result would seem to dispose of the theory advanced that white lead should be applied with longer oil reductions. If the amount of oil and not the amount of pigment should determine the service of a paint, would not a pigment such as asbestine, which requires enormous quantities of oil, form a paint more durable than white lead or any of the other white base pigments? We all know, however, that this is not wholly the case, and, moreover, we must look at the question in a practical manner, for the hiding power of a paint is one of the most important properties.

The percentage of lead carbonate in corroded white lead determines its hiding power, while the percentage of hydrate determines the oil-carrying capacity. When the amount of carbonate runs to 80 per cent., the lead has a high gravity and takes only $3\frac{1}{2}$ gals. of oil to a hundred pounds of paste lead to produce an easy-spreading paint that will have good hiding properties. When the amount of carbonate in corroded white lead drops to 60 per cent. and the hydrate reaches 40 per cent., difficulty in grinding is observed, even if additional oil is added. Such a product is likely to harden and become gummy in the package, and upon thinning 100 lbs. of paste for application 6 gals. of oil are required and the product has only slight hiding power. Corroded white lead that contains about 70

*Paper prepared for the convention of the Pennsylvania State Association of Master Painters, Scranton, Pa., Jan. 18, 1912.
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per cent. lead carbonate and 30 per cent. lead hydrate is probably the best grade that can be obtained; its oil absorption is medium and its working properties and hiding power excellent.

The claim has been advanced that the application of long oil leads in repainting work is desirable, on account of the penetration into the old paint that can be secured from the newly-applied paint, both amalgamating to form one solid film. If this phenomenon really took place under such conditions, a cross section of the film produced would probably appear under the microscope as one solid mass of pigment and oil. As a matter of fact, this is not the case, as an examination of photomicrographs will show.

It is very generally admitted that tinted paints are far more durable than white paints. In the article under discussion, the claim is made that the increased durability of tinted paints is due entirely to an increase of oil brought to the white paint by the coloring pigments, all of which have rather high oil-carrying properties. As a matter of fact, however, the amount of oil carried into a white paint by one or two per cent. of tinting color is too small for consideration and is quite insufficient to give the result claimed above. White leads made by various processes take up varying amounts of oil, 100 pounds of some paste leads requiring only $3\frac{1}{2}$ gallons of oil, while in other cases leads made by different processes require as high as 6 gallons of oil to produce paints of a relative consistency. Upon exposure of such leads, there seems to be no material difference in the way they wear. This result would further indicate the fallacy of claiming that the extra durability obtained from tinted paints is due to the slight increase of oil brought to them as a contribution from the coloring matter used. We must attribute the greater durability of tinted paints, therefore, to the nature of the added tinting pigments and to the differing physical and chemical properties which they bring to the white base.

The carbonate pigments, such as lead carbonate, calcium carbonate, and barium carbonate, will all chalk when painted out and exposed to the elements. This chalking seems to be a distinct feature of the carbonate pigments. While it is true that certain other pigments which are not carbonates chalk quite heavily, it is furthermore true that the exception proves the rule. Pigments which are not carbonates, but which have other radicals, and which will probably be more readily recognized if called by their trade names, such as red lead, zinc white, litharge, etc., do not possess chalking tendencies, and they form paints which remain hard and glossy under long exposure. When either carbonate pigments or oxide pigments are reduced with short or long oil reductions, the same conditions hold true. It would become at once apparent, therefore, that if the chalking tendencies of the carbonate pigments are to be overcome and corrected, or the excessive hardness of the oxide pigments is to be reduced, a mixture of the two in the correct proportions should solve the problem. As a matter of fact,

mixtures of this type do not become excessively hard, nor do they chalk to any great extent, and, although this principle was long ago discovered and has been used for years by progressive painters, it must be stated over and over again in order to convince those who are not thoroughly familiar with the results of paint tests.

After considering the present practice of some of the leading members of the association, and summing up the results obtained from practical tests made throughout the country, the writer has formed the conclusion that the paint best suited to withstand service is a tinted paint made of a proper mixture of pigments, carefully ground together and applied by a painter, for even the best paint made must be applied with skillful hands, backed by intelligence, if the best results are to be obtained.

The gold production of New South Wales for 1911 was 215,274 ounces, worth \$3,750,000.

The production of pulp wood in Canada for 1910 amounted to 1,541,628 cords, valued at \$9,795,196. Of this 943,141 cords, value \$6,210,042, were exported (27,508 cords more than in the preceding year), and 598,487 cords, value \$3,585,154, were consumed in Canadian mills. Fifty-one pulp mills in the Dominion reported using 23,642 cords less than the consumption for 1909, but the increase in the average price per cord brought up the value of the industry to \$121,074 more than the previous year. The average consumption of pulp wood per mill during 1910 was 11,735 cords, compared with 12,442 cords in 1909. The largest mills are in Ontario and these used an average of 14,037 cords each. The average consumption per mill in Quebec was 13,710 cords; in Nova Scotia 4,934, and in New Brunswick 3,783 cords.

The municipal authorities of Montevideo, Uruguay, have in preparation the draft of an ordinance whose provisions, when operative, will tend to prevent the employment of toxic substances in many articles of everyday use. Among the most important features are those which regulate the quality of tin used in the manufacture of various utensils. By this ordinance the proportion of lead is reduced to 5 per cent in the measures which the analyzers use, and in all other utensils practically pure tin is demanded, its purity to be proved by official analyses before they can be placed on sale. It also provides that house paints, paper, tapestries, etc., shall not be colored by any material containing arsenic. Conserve boxes and jars must be hermetically sealed and soldered on the outside only, to avoid the entrance of lead; and further, it is provided that the mechanism of siphons shall show no scratches and that they shall bear the name of the soda manufacturer as well as the seal of the analytical office, to prevent any substitution of the contents.

METHODS FOR THE UTILIZATION OF WOOD WASTE.*

By GEORGE WALKER.

Starting with logging operations in the forest, there is a vast amount of waste in the shape of branches, tops and roots of trees. The stumps of the resinous wood trees contain considerable quantities of resinous matter, and some attempts have already been made to utilize them by destructive distillation and by extraction with steam and solvents. This has been attempted in some of the western and southern states, more especially the latter, where the stumps are much richer in resin. The waste of the saw-mill consists of slabs, edging and saw-dust which it has been proposed to submit to destructive distillation. There are, however, many obstacles to any profitable employment of such waste in this way. Such waste constitutes the poorest parts of the tree so far as the yield of distillation products, such as methyl alcohol, acetic acid, and tar are concerned, and the residual charcoal is for the most part in such a fine state of division and the mills so distant from a market that it seems impracticable to utilize it excepting for fuel in the carbonization of fresh quantities of wood. In the case of the mills, sawing hard wood, such as oak, beach, birch, etc., the yield of distillation products need not, with the proper apparatus, be less than that obtained by the wood distillers of New York and Pennsylvania, who use almost exclusively beech, birch, and maple wood.

The distiller of saw-mill waste would, however, be heavily handicapped by the unsalability of his charcoal, which is the most important source of profit to the ordinary wood distiller, amounting to about \$2.40 for each cord of wood distilled, and yielding sufficient revenue to almost pay for the wood.

In the case of the soft woods the handicap becomes still heavier owing to the fact that such wood yields less than half the quantities of acetic acid and methyl alcohol obtained by the ordinary wood distiller. A comparison of the two methods shows that whereas the ordinary wood distiller obtains a total value of about \$8.10 per cord of wood distilled, the distiller of saw-mill waste would only obtain a total value of \$2.85, and the expense for labor, etc., in both cases would be about the same.

It is contended that some turpentine can be obtained from mill waste. This is only true as regards the waste obtained in sawing long-leaf yellow pine, and only then in exceptional cases, viz., in the case of mills using the wood of trees which have been boxed for turpentine, and on the logs which have the so-called "box faces," or that portion of the trunk on which the oleo-resin has collected and hardened after the turpentine extractor has abandoned it. The utilization of the saw-dust, however, deserves some attention.

A small saw-mill town in Canada needed light, and as wood-gas was attracting some attention at the time,

the owner of the mill, sawing 120,000 ft. of lumber per day, and producing large quantities of saw-dust and other waste wood thought some of it could be utilized for making gas. I undertook to do this and erected a plant for the purpose. The plant consisted of two benches, of five retorts each, capable of distilling ten tons of saw-dust per day. The retorts were of cast iron, 1½ ins. thick, 12 ft. long, and 12 ins. in diameter, and provided with Archimedean screws having flights of cast iron on a 2½ in. shaft. The saw-dust was delivered to the screw in the retort from a hopper at the front end, from which the saw-dust was passed through vertical 6 in. pipes by means of screw conveyors. The rate of speed of the main screw was regulated so that a thin layer of saw-dust continually passed along the bottom of the retort from front to rear, and was carbonized on its passage and delivered at the rear end into a main provided with a screw conveyor by which it was delivered to an air-tight sheet iron car. There was a vapor main common to all the retorts at the rear end, and from this main the vapors and gases were passed to a condenser. The system was provided with a gas exhauster and scrubber, and the pressure in the retorts was maintained by this means as near zero as possible. The saw-dust used was made from Canadian pine and was dried in a special steam dryer before being delivered to the retorts. As the object of the plant was the production of illuminating gas but little attention was paid to the residual products, which were insignificant in quantity and not worth the expense of refining. I think some similar process might be used for mill waste by passing all the waste wood through a "hog," and carbonizing it as the process can be carried on automatically with a minimum of labor. I found that the dry saw-dust contained sufficient resinous matter to bind the particles together, when warmed and powerfully compressed, and a compressor was erected for this purpose and a considerable quantity of briquettes made, which seemed when first made of good quality, but unfortunately there was not sufficient resinous matter in the saw-dust to exclude moisture, and the hygroscopic nature of the dry saw-dust soon led to swelling and crumbling of the briquettes made.

It must be remembered that the slabs, edgings and saw-dust are derived from that part of the tree poorest in resinous matter, and in the case of the saw-dust, nearly all of the turpentine it contained while in the tree evaporates whilst in process through the mill in consequence of its fine state of division.

In ordinary wood distillation, when wood is slowly distilled, there is a point when a temperature of 275° C. has been reached when the flow of volatile products through the condenser almost ceases and the exit pipes connecting the retorts with the condensers, commence to cool. Before reaching this point nearly all the acetic acid and methyl alcohol have distilled over, but very little tar, and if the distillation be then stopped and the retort cooled and opened, the wood will be found of a dark red color and containing nearly all the tar.

*From the Journal of the Society of Chemical Industry.

Some time between the years 1870 and 1880, a process was carried on in New York by the late Dr. Squibb, wherein advantage was taken of the fact just described, for the production of a red charcoal which he termed "tinder wood." The wood used was oak brought down the river in boats and split into ordinary kindling wood size and then distilled in a special oven until the point was reached at which the wood was converted into red charcoal. This red charcoal was then placed in paper bags and sold for kindling wood, and the acetic acid and methyl alcohol refined by the ordinary methods. It proved an excellent material for kindling fires, but domestic prejudices destroyed the industry. Besides pyroligneous acid, methyl alcohol and charcoal, there is produced by the distillation of wood a quantity of tar, amounting in the case of the hard woods to about seven per cent of the weight of the wood or about 25 gals. per cord. This tar is not utilized at present for any other purpose known to me except for fuel for the retorts of steam boilers, and for the recovery of the wood alcohol which it contains, but it may be further distilled and products of value obtained from it.

In the wood distilling plants this tar is distilled by means of direct or indirect steam for the recovery of methyl alcohol, and a considerable quantity of light oil distills over with the methyl alcohol, the tar remaining in the still being called "steamed tar" by the wood distillers. I have distilled this steam tar in large cast iron stills containing about 2,500 gals. each and have produced therefrom about 30 per cent of heavy oil having a specific gravity of 1.020 to 1.060 and a boiling point of 200° to 300° C. and a residue of about 60 per cent of pitch suitable for making briquettes of artificial fuel, when mixed with 90 to 92 per cent of coal dust and compressed. The heavy oil may be sold as a wood preservative either by itself or mixed with dead oil of coal tar, or it may be treated with caustic soda and sulphuric acid for the production of pure wood creosote. The oil coming over at the end of the tar distillation contains a large percentage of wood paraffin which, when the oil is used for preserving timber, enters the pores of the wood and becomes a wax-like solid on cooling, thoroughly preventing the access of water to the wood and at the same time preventing decay.

This oil containing paraffin, has a great advantage over coal tar oils containing naphthalene inasmuch as the paraffin is not volatile as the naphthalene is. A curious thing connected with the distillation of wood tar is its liability to boil over near the end of its distillation. In this respect wood tar behaves in an entirely different manner from coal tar, the former always boiling over, if at all, at the end of the distillation, whilst the latter boils over, if at all, at the beginning. At least 500,000 bbls. of wood tar are produced annually by the wood distillers of the United States. This could be collected at some central refinery and there used for the purpose I have described,

and might form the basis for a large and profitable industry. The light oil produced from the tar by steaming, is a reddish brown liquid and has a sp. gr. of 0.920 to 0.960. When distilled with steam and purified by treatment with caustic alkali, it is an almost colorless liquid of about 0.880 specific gravity and has a very penetrating odor. In its purified condition it is a powerful solvent and mixes with nearly all oils. I discovered in 1898 that this oil is an excellent solvent for pyroxylin and during the past year I have purchased from the wood distillers about 100,000 gals. of it for this purpose.

In the northern states the waste of wood has been caused by the methods of the saw-mill man, but in the southern states the greatest waste is due to the operations of the turpentine extractor, supplemented by the operations of the long-nosed pig of the farmer which has a fondness for the roots of the young yellow pines. What is known as the naval stores industry commenced about 1845 in North Carolina and for some years was confined to the manufacture of pine tar and gum turpentine, the latter being exported to England and used there for making resin and turpentine oil. Since that time the industry has progressed with great rapidity and last year the products amounted in value to at least \$40,000,000, requiring for their production the destruction of 1,500,000 acres of virgin forest.

This rapid destruction of forest has caused a scarcity of trees suitable for the industry, and there has consequently been a large increase in prices.

The unscientific methods of the turpentine extractor, mean destruction of the tree in from four to five years, and unless the turpentine is produced in connection with, or near, a saw-mill, the trees are blown down and very soon decay and become useless for timber. After the tree has been apparently killed by the turpentine extractor, the bark and sap-wood rapidly decay in that warm moist climate, but a resinous central portion remains which is called "light wood" because it burns with a luminous flame and has been and is now used as lighting material. The method of the formation of "light wood" is unknown, but it seems certain that the resinous matter by some natural process concentrates in the center of the tree after it is apparently dead.

The light wood formed as described, is very rich in oleo-resin, in some cases amounting to 40 per cent of the weight of the wood. When this wood is destructively distilled, it yields considerable quantities of an oil resembling that produced by the destructive distillation of rosin, besides a quantity of oil of turpentine, also small quantities of acetic acid and methyl alcohol and a large quantity of uncondensable gas of high illuminating power. The relative quantities of these products depend upon the method of heating the retorts, and the rapidity of distillation. Uncondensable gases are formed largely from the resinous matter at the expense of the oils.

I have been distilling this wood for several years in South Carolina in steel cylindrical retorts having a capacity of about one cord each. As the plant is too far from a charcoal market to admit of this material being profitably transported, it is used for fuel, together with the uncondensable gases, for the distillation of another charge of wood. At the commencement of the distillation a small fire is made under the retort and live steam admitted to the wood in its interior. The action of steam and fire is continued until all the oil of turpentine has distilled over when the steam is shut off, and the heavier oils distilled over at a higher temperature. At the end of the distillation steam is injected into the charcoal in the retort after the water surrounding the condenser has been run out. By this means the heavy oily matter remaining in the condenser which would contaminate the turpentine oils and render their subsequent refining more difficult, is blown out and at the same time the steam serves to quench any fire which might occur in the charcoal when being drawn from the retort. This distillation is supplemented by the action of a steam jet exhauster which connects with the end of the condenser and serves to produce a partial vacuum in the retort and eliminates pressure of vapor in the retorts and consequent loss of condensable products by decomposition. All the uncondensable gases are passed through the exhauster and are pushed by it through a series of fine copper screens in an upright cast iron cylinder or scrubber whereby the globules of tar enclosing the gas are broken up and the tar removed, the gas in its purified condition being then conducted to the retort furnaces and burned for fuel.

The heavy oils produced by the distillation of the wood are distilled in cast iron stills, a residue of elastic glossy black pitch amounting to about 25 per cent of the weight of the oil remaining in the still. The distillate from this operation consists of a light oil resembling turpentine, but having a specific gravity of about 0.880, and an oil heavier than water containing about 20 per cent of creosote and a large quantity of wood paraffin.

As is well known, there is a process in use in the south which consists in grinding or "hogging" the light wood or stumps and then submitting the ground wood to the action of live steam in closed vessels, whereby the turpentine oil is carried over by the steam into a condenser and afterwards refined and sold as wood turpentine.

In 1905 it occurred to me that the resin contained in the light wood after the extraction of the turpentine by steam could be recovered by a process of extraction with a volatile solvent based on the principle of the well known soxhlet extractor, and after a series of experiments in the laboratory and with an experimental apparatus constructed on a working scale to determine yields and costs, I devised and constructed a plant at Conway, South Carolina, to carry out my process. In this process the finally divided light wood is subjected to the action of live steam in large steel

cylinders for the extraction of the turpentine, and the wood, minus the turpentine, treated with a volatile solvent for the recovery of the rosin. This apparatus is now producing rosin at the rate of about 200 bbls. per week and a considerable quantity of turpentine. As this process produces about five times as much rosin and turpentine in 12 hours as the same quantity of wood produces in four years by the old method of "boxing" the trees, it is probable that in the near future this method of making rosin and turpentine will supersede the old one.

Of course the future of such an industry depends upon the quantity of raw material (light wood) to be obtained. Light wood, as I have before stated, is the debris or waste of the naval stores industry, but in spite of the fact that considerable quantities of light wood are used for railroad ties, it is considered by competent observers that there is enough of this waste material remaining in the southern states to supply the wants of the world in rosin and turpentine for many years. After the extraction of rosin and turpentine from the "light wood," the extracted wood forms an excellent material for the manufacture of wood pulp. Probably at some future time the lumber, naval stores, and wood pulp industries will be carried on together and this will be accomplished by the acquisition of a yellow pine forest, the annual growth of which will be sufficient to provide for the needs of a saw-mill, an extraction and a wood pulp plant.

This forest could be placed in charge of an experienced forester and the supply continually renewed. An estimate of the area of the forest required would be based on the fact that twenty-five years are required for the tree to reach its proper size, and the number of cords of "light wood" can be closely approximated. The conversion of the trees into light wood after being felled, requires a period of from 5 to 10 years, and light wood produced in this way from the "untapped" trees, would have several advantages. The trees could be kept close to the ground and the heavy resinous butts which are often rejected by the lumbermen on account of the difficulties encountered in sawing them, would all be utilized.

By the method described, the light wood produced would be free from decayed and partially burnt material and would contain more resinous matter than the light wood now available and would produce more turpentine and lighter colored rosin. It would also save an enormous quantity of wood now destroyed in the ordinary process of "turpentinizing" and would, I think, place the naval stores, the lumber, and the wood pulp industries on a permanent basis.

The present estimates for the sugar production of Cuba for 1912 run slightly higher than they did a few weeks ago. The more conservative still maintain their estimate of 1,600,000 to 1,700,000 tons, while the most prevalent and competent estimates run from 1,800,000 to nearly 1,900,000. The consensus of opinion is that the production will go well over 1,800,000 tons.

POTASH SALTS FROM SEA WEED.

By G. V. GREEN AND H. S. JOHNSON.

This work was undertaken to determine the possibility of obtaining potash salts and iodine from certain sea weeds in such quantity as to make the process one which would be commercially feasible and also to determine the products yielded on destructive distillation of such material with the idea that some of these products may be of value.

METHOD OF PROCEDURE.

The various weeds were analyzed for: (1) Moisture, (2) Volatile matter, and (3) Ash.

The ash was then lixiviated with water and the water extract was evaporated to dryness and the residue weighed. The residue was analyzed for its various constituents. A second sample of weed was lixiviated with boiling water and the extract evaporated to dryness and weighed. This residue tallied closely with the residue obtained from water lixiviation of the ash. The residue of ash remaining after extraction with water, was dissolved in hydrochloric acid and the various constituents determined. There yet remained a residue from the hydrochloric acid extraction. This was weighed as silica.

Iron and alumina were precipitated by ammonia; the hydroxides obtained were ignited and weighed as combined oxides. Calcium was determined as oxalate and weighed as the oxide. Magnesium was weighed as the pyrophosphate. Sulphates were determined by precipitation with barium chloride. Carbonates were titrated with standard hydrochloric acid. Chlorides were titrated with standard silver nitrate, using potassium chromate as an indicator. Carbonates were first decomposed with nitric acid. Sodium arsenate as an indicator gave excessively high results in the titration of chlorides and had to be rejected as an indicator. We were unable to determine the combined halides by the Jannasch method; neither were we able to determine iodine by titration with potassium permanganate. Organic impurities gave too high values for the iodine.

We finally used colorimetric methods for the estimation of iodine and bromine. In detail these methods are as follows:

For iodine:—

To an aliquot part of the solution containing the iodides, add an equal amount of sulphuric acid (50% H_2SO_4 -50% H_2O). Then add bromine water (.2 cc. Br. in 20 cc. HCl and made up to one liter) drop by drop until maximum coloration is produced. This reaction was carried on in a graduated tube such as is used for determining carbon by color. Five cc. standard solution potassium iodide containing 0.001 grams iodine per cc. was treated in another tube with the same reagents. The color of the two solutions was made the same by dilution with distilled water. The ratio between the volumes in the two tubes was read

off and the amounts of iodine in the unknown sample calculated.

Bromine:—

The method of procedure was the same as for iodine, save that instead of bromine water an excess of saturated solution of chlorine water was used to displace the bromine. The standard solution for comparison contained 0.001 grams of bromine per cc. An excess of chlorine water was added to form iodine chloride, thereby destroying the color produced by iodine. These methods are used for the rapid estimation of iodine in sea weed ash. The method for iodine is said to be very accurate. The iodine in the mother liquors from the crystallization of the salts in the weed, was determined by this method, owing to the fact that the volumes of liquor were too small for distillation and sublimation.

The weeds were destructively distilled in a copper retort and the products of decomposition were condensed and caught in suitable receivers. Water was added to each charge of weed to facilitate distillation. The residue in the still was black, owing to incomplete burning of the carbon. As it was impossible to produce a white or even gray ash in the retort, the black residue was removed and heated in an open iron pan. The result was a gray ash, it being impossible to produce a white ash without fusing the material. We conducted a current of air thru the retort in hopes of oxidizing all the carbon, but the ash obtained was not as gray as that produced by heating in an open iron pan where it was possible to constantly stir the ash. Had the retort been provided with a mechanical stirrer, the method no doubt would have been successful. It was essential that the residue from the retort be heated still more strongly, because the water extract from it was of a reddish-brown color.

The ash was lixiviated with boiling water for one hour. Two more extractions with boiling water were made, each of one-half hour duration. The extracts, after combining and filtering to remove suspended matter, were concentrated to a point of crystallization. The first crop of crystals was recrystallized and the mother liquor was added to the original mother liquor. Two more crops of crystals were obtained from this liquor. The final mother liquor was treated for iodine. A qualitative analysis was made of each crop of crystals and each constituent was then determined quantitatively.

We examined three samples of weed; the first came from the Atlantic Ocean, the other two from the Pacific. We will now separately discuss each weed.

ATLANTIC WEED.

This weed, called sea grass, was gathered at Greenport, L. I., New York, in November, 1910. It grows upon rocks and in shallow water. It is completely submerged at all times. Rough weather tears the weed from the rocks and casts it upon the shore. Thorpe in his "Dictionary of Applied Chemistry"

states that this species contains no iodine. Our analysis of the weed is as follows:

	Percent.
Moisture	13.86
Ash	31.06
Volatile matter.....	55.08
P. C. ash water soluble.....	34.57
Water sol. matter in weed.....	6.64
Silica	9.26
CaCO ₃	13.04
Al ₂ O ₃ and Fe ₂ O ₃	1.54
MgSO ₄	2.54
NaCl	0.97
KCl	3.40
Iodine	trace
Bromine	0.075

The ash obtained from this weed was white and feathery. An inspection of the analysis will show that the weed is high in calcium carbonate and silica, while it is low in potassium and sodium chloride. We account for the presence of insoluble calcium carbonate by the fact that it may have existed in the weed as the bicarbonate. When an aqueous extract of the ash was boiled, a precipitate of calcium carbonate settled out. For the most part the constituents of this weed are insoluble in water. We were unable to detect any iodine in a gram sample of the ash. This apparently bears out the above statement made by Thorpe.

We found that it would be impossible to obtain the inorganic constituents of this weed or any of the other weeds by a simple water extraction. The organic impurities were extracted by the water in sufficient quantity to impart to the residue a blackish-brown color. Neither would filtration thru bone-char nor ignition, effect a complete removal of organic matter from the salt residue. The removal of organic matter by ignition had the added objection in that the salt was fused and partly volatilized. It is, therefore, evident that it is best to ignite the weed to as white an ash as is possible without fusion, and then to extract the soluble matter with hot water. By this means we were able to secure a clean white salt. This same may be said regarding the two other weeds upon which determinations were made.

The data concerning the experimental treatment of the weed were as follows:

Weight of weed taken.....	3.00 lbs.
Weight of ash obtained.....	1.84
Weight of distillate and vol. matter.....	1.16
Per cent ash.....	61.30%

The per cent ash is almost double the true value owing to its incomplete oxidation in the retort.

Weight of ash lixiviated.....	0.35 lbs.
Per cent KCl in ash—3.40 is equal to.....	0.0119 lbs.
Weight of crystals obtained.....	0.01
Analysis of the crystals:	
K ₂ SO ₄	25.32%
CaCO ₃	12.81
Na ₂ SO ₄	9.73
KCl	44.18 equals 0.0044 lbs.
NaCl	6.12
Per cent yield of KCl.....	37.00%

The results show that there was a very poor yield of crystals. In fact they could scarcely be called crystals as their appearance resembled that of a coarse powder. On attempting to dissolve the crystals for recrystallization it was found that they were difficultly soluble in hot water and almost insoluble in cold

water. Attempts to secure three crops of crystals were futile.

While we were unable to find any iodine in a one gram sample of the ash, an appreciable amount was estimated in the mother liquor from the crystals. We attribute this to the fact that there was a greater concentration in the mother liquor, thus making it possible to detect its presence.

Distillation Products.—Water was added to the weed to aid in its distillation. The distillation was, of necessity, conducted slowly, owing to the fact that a rapid rise in temperature caused a rapid evolution of uncondensable gases. The first condensates appeared at 85 degrees C. These were small in amount. The temperature rose to 98 degrees where most of the distillates came over. As the temperature rose above 100 degrees the amount of tarry matter coming over came more pronounced. The color of the distillates varied from a pale yellow at 100 degrees, to a brownish-black at 360 degrees, indicating an increase in tarry matter. In the fraction collected at 120 degrees a faint odor of alcohol was noticed but no attempt was made to recover it. In no other fraction was there any indication of the presence of alcohol.

None of the gases evolved during the distillation were rich enough to burn. This statement also applies to the two Pacific weeds.

DATA ON THE DISTILLATION PRODUCTS		
Fraction.	Temperature.	Comments.
1	85 to 98C.	Pale yellow.
2	98 to 110	Watery
3	110 to 125	Red tinge
4	125 to 145	No sharp change in color,
5	145 to 160	color gradually became
6	160 to 185	darker, due to increase
7	185 to 200	in tarry matter
8	200 to 240	Very dark owing to
9	240 to 310	increase in tar, very
10	310 to 360	small amounts.

These distillates were added to form three portions, in the following manner:

First portion.....	85 to 110C.
Second portion.....	110 to 200
Third portion.....	200 to 360

An attempt was made to fractionate the above portions, but a very surprising result was obtained—practically all of each portion came over at 98°. In each case there remained behind a small amount of coke. We explain this behavior of the distillates by the fact that water was being continually formed thruout the distillation of the weed. Part of this water was due to the original moisture in the material and part to the formation of water by the combustion of the hydrogen and oxygen in the weed.

THE FIRST PACIFIC WEED.

This weed, known as *Nereocystis Leutkeana*, was gathered in December, 1910, from Deception Pass, an arm of Puget Sound. It was growing in water about sixty feet deep. The weed consists of a long stem varying in diameter from one to six inches at the top, and tapering to a diameter of a fraction of an inch at the other extremity. The shape of the stem resembles that of a carrot. The top of the stem terminates in an air bladder which serves to float it. The leaves

radiate from this bladder and float upon the water. This first sample consisted of stems only. It was received in Chicago by express a few days after being gathered, and was immediately dried in an oven. Before drying there were no salts visible on the stem, but after drying they appeared in great abundance. The amount of effloresced salts was so great that it fell off in scales.

An analysis of the weed follows:

	Per cent.
Moisture	1.82
Ash	68.40
Volatile matter.....	29.78
Water soluble ash.....	93.40
Water sol. matter in weed.....	60.45
Silica	0.30
Al ₂ O ₃ and Fe ₂ O ₃	1.09
CaCO ₃	2.52
MgSO ₄	1.95
Bromine	0.27
Iodine	0.23
NaCl	8.01
KCl	52.71

An inspection of the analysis will show that this weed is high in an ash which is for the most part soluble in water; that it is high in potassium chloride, and low in calcium carbonate and silica; that the bromine content is slightly in excess of the iodine. The ash of this weed had a strong tendency to fuse upon ignition and it was impossible to obtain better than a dark gray ash. Experimental data concerning the treatment of the weed were as follows:

	Pounds.
Weight of weed taken.....	0.62
Weight of ash obtained.....	0.40
Weight of distillate and vol. matter....	0.22
Per cent ash.....	64.50

The amount of distillate coming over was very small, amounting to 0.09 pounds. For the most part it consisted of tar.

Weight of ash lixiviated.....	0.089 lbs.
Per cent KCl in the ash (77.52%) equals	0.068
Weight of crystals, first crop.....	0.075
Weight of crystals, second crop.....	0.005
Analysis of the crystals:	

FIRST CROP.	
Water	4.52%
K ₂ SO ₄	4.66
KCl	89.16 is equal to 0.0628 lbs.
NaCl	1.13

SECOND CROP.	
Water	1.56%
K ₂ SO ₄	11.85
KCl	83.59 is equal to 0.0642 lbs.
NaCl	2.52

Total KCl in the crystals.....0.067 lbs.

Per cent yield of the KCl = $0.067/0.068 = 98.7\%$

The first crop of crystals was characterized by the large amount, and their high purity in potassium chloride. No difficulty was experienced either in obtaining either the first or second crop. The second and third crops were combined owing to the small amount of the latter. This combined crop was inferior to the first in purity, owing to the presence of sulphates.

The distillation products were water and tar which came over at 125° C. to 360. We were unable to find any other constituents in the distillates.

THE SECOND PACIFIC WEED.

This weed is of the same species as the previous one. It was gathered three months later from the same locality. The sample received consisted of stems,

bladders, and leaves, and had been oven dried previous to shipment. The analysis of the weed is as follows:

	Per cent
Moisture	8.07
Ash	42.82
Volatile matter.....	49.11
Water soluble ash.....	87.80
Water soluble matter in the weed.....	32.35
Silica	0.90
Al ₂ O ₃ and Fe ₂ O ₃	2.00
CaSO	2.03
CaCO ₃	0.87
MgSO ₄	1.65
Iodine	0.10
Bromine	0.08
NaCl	3.02
KCl	32.12

An inspection of the analysis will show that the moisture content is higher; that the ash, water soluble ash, calcium carbonate, magnesium sulphate, iodine, and alkali chlorides are lower than in the case of the first sample of this same weed.

Experimental data concerning the treatment of this weed were as follows:

Weight of weed taken, pounds.....	3.00
Weight of the ash, pounds.....	2.15
Weight of the distillate, pounds.....	0.53
Weight of the volatile matter.....	0.32
Per cent ash.....	71.66

This does not represent the true value of the ash, owing to incomplete oxidation in the retort.

	Pounds.
Weight of ash lixiviated.....	0.70
Per cent KCl in the ash (75.05%) equals	0.52
Weight of crystals, first crop.....	0.21
Weight of crystals, second crop.....	0.14
Weight of crystals, third crop.....	0.04

Analysis of the crystals:

FIRST CROP.	
Water	12.34
K ₂ SO ₄	3.62
KCl	81.48 = 0.171 lbs.
NaCl	1.99

SECOND CROP.	
Water	7.70
K ₂ SO ₄	12.85
KCl	76.63 = 0.107 lbs.
NaCl	2.41

THIRD CROP.	
Water	4.84
K ₂ SO ₄	14.90
KCl	73.32 = 0.029 lbs.
NaCl	6.38

Total KCl in the crystals.....0.308 lbs.
Per cent yield KCl = $0.308/0.52 = 59.4\%$

Three crops of crystals were obtained from lixiviation of the ash from this weed. The potassium chloride content decreases with each succeeding crop of crystals, while the amount of potassium sulphate and sodium chloride increases. This is to be expected from the fact that the purer crystals are found in the first crystallization. The larger crop was obtained at first; the second crop amounted to two-thirds that of the first, while the last amounted to almost nothing.

The distillation of this weed was conducted in the same manner as in the case of the previous weeds. The character of the distillates was, for the most part, watery. A small amount of tar floated on the surface of the distillates in patches. Owing to the small volume and nature of the products no attempt was made to fractionate them. It was upon this weed that we made the unsuccessful attempt to oxidise the ash by blowing air through the retort.

COMPARISON OF THE EXPERIMENTAL RESULTS.

In only one of these weeds, namely the Atlantic, do our analyses show the true moisture content. This weed was dried upon the rocks in the sun. In the case of the Pacific weeds the moistures were obtained after the samples had been previously dried in ovens. According to Balch, 15 per cent is a fair moisture content for sun dried weed. This same author states that about 90 per cent of the freshly gathered weed is water.

Ash.—This constituent is lowest in the Atlantic weed, which goes to show that this species is a poor collector of mineral matter. The two Pacific samples contained 68 and 42 per cent of ash, respectively. Inasmuch as these weeds are of the same species and came from the same locality, it would seem that their

the results obtained. The first sample of Pacific weed consisted of stems only, the second consisted of stems, bladders and leaves.

The potassium chloride content increases with the per cent of ash. From our results it would appear that the stems of the weed assimilate the largest amount of potassium salts.

Iodine.—It is evident from our results that some weeds do not gather any iodine. As in the case with potassium chloride, the stems of the Pacific weed gathered the largest amount of iodine. Our results seem to show that a high silica, alumina, iron, calcium and magnesia content is to be accompanied by small amounts of potassium and iodine. As may be expected from what has already been stated, the first Pacific weed yields the purest and largest amount of

TABLE I.—COMPARATIVE SUMMARY OF RESULTS.

AN ANALYTICAL SUMMARY OF THE THREE WEEDS.													
Weed	Moisture	Ash	Volatile Matter	SiO ₂	$\frac{H_2O_3}{Fe_2O_3}$	CaCO ₃	MgSO ₄	Bromine	Iodine	NaCl	KCl	Water Sol. Ash	Water Sol. Weed
Atlantic	13.86%	31.06%	56.08%	9.26%	1.54%	13.04%	2.54%	.075%	Trace	.97%	3.40%	34.57%	6.64%
1st Pacific	1.82	68.40	29.78	.30	1.09	2.52	1.95	.27	.23%	8.01	52.71	93.40	60.45
2nd Pacific	8.07	42.82	49.11	.90	2.00	2.02	1.54	.08	.10	3.02	32.01	87.80	32.35

ANALYSIS OF CRYSTALS.

Weed	Crop	Mois're	K ₂ SO ₄	KCl	NaCl	CaCO ₃	Na ₂ SO ₄
Atlantic....	1st	1.12%	25.32%	44.18%	6.12%	12.81%	9.73%
1st Pacific..	1st	4.52	4.66	89.15	1.13		
"	2nd	1.56	11.05	83.59	2.52		
2nd Pacific..	1st	12.34	3.62	81.48	1.99		
"	2nd	7.70	12.85	76.63	2.41		
"	3rd	4.84	14.90	73.32	6.38		

% YIELD KCl FROM ASH.

Weed	Weight Crystals	Crop	Wt. KCl in Ash	Yield KCl, lbs.	% Yield KCl
Atlantic.....	.01 lb	1st	.0119lb	.004lb	37.00
1st Pacific....	.0628	1st	.068	.067	98.70
"	.0042	2nd			
2d Pacific	.21	1st			
"	.14	2nd	.52	.308	59.04
"	.04	3rd			

ANALYSIS OF AIR DRIED WEED.

Name of weed...	Results Obtained by Balch						Results Obtained by Green & Johnson					
	<i>Pelagophycus Porra</i>	<i>Nercocystis Leutkeana</i>	<i>Macrocyctis Pyriferia</i>				<i>Nercocystis</i> 1st Shipment	<i>Nercocystis</i> 2nd Shipment			Sea Grass from Atlantic	
Part of weed	KCl% Iodine	KCl% Iodine	KCl% Iodine				KCl% Iodine	KCl% Iodine			KCl% Iodine	
Stems.....	30.80 0.19%	55.10 0.24%	26.40 0.20%				52.71 0.23%	32.12 0.10%			3.40 00	
Leaves.....	15.00 0.21	30.64 0.05	18.60 0.14									
Bladder.....	48.85 0.10	61.10 0.06	35.28 0.21									
							Stems only	Whole weed			Whole weed	

ANALYSIS OF THE CRYSTALLIZED SALTS.

Name of weed...	Results Obtained by Balch						Results Obtained by Green & Johnson					
	<i>Pelagophycus Porra</i>	<i>Nercocystis Leutkeana</i>	<i>Macrocyctis Pyriferia</i>				<i>Nercocystis</i> 1st Shipment	<i>Nercocystis</i> 2nd Shipment			Sea Grass from Atlantic	
Part of weed	KCl% Iodine	KCl% Iodine	KCl% Iodine				KCl%	KCl%			KCl%	
Stems.....	89.90 0.55%	88.40 0.40%	88.60 0.64%				Crop	Crop			Crop	
Leaves.....	49.24 0.85	69.90 0.117	85.00 0.70				1st 2nd	1st 2nd 3rd			1st	
Bladder.....	98.72-66.60	 0.11	98.99 0.54				89.16 83.53	81.48 76.63 73.32			39.58	
Effloresced salts, KCl %.....	98.72%	98.30%	99.23%				Stems only	Whole weed			Whole weed	

mineral content is influenced by three factors, viz.: (1) Season of the year, (2) Age of the weed, and (3) Part of the weed taken for analysis. The Pacific weeds were gathered at different seasons of the year, one in December and the other in the early spring. Again, one weed may have been the older, in which event it would be much richer in salts, due to the fact that the longer the weed grows the greater its store of mineral matter becomes. This particular species reaches maturity in twelve to fifteen months, at the end of which time it dies. Further, the part of the weed taken for analysis doubtless has a bearing upon

potassium chloride. The low yield of potassium chloride (59%) obtained from the second Pacific weed, may be explained by the fact that the oxidation of the ash in the open pan caused the material to fuse. This rendered a complete extraction of potassium salts impossible. We are at a loss to account for the low yield (37%) of potassium chloride from the Atlantic weed. This weed yields a higher per cent of sodium chloride and potassium sulphate than do the Pacific weeds.

The species of sea weed, known as sea grass, which came from the Atlantic, is far inferior in every respect

to the giant kelp of the Pacific; and the stems of the giant kelp are a richer source of potassium and iodine than are all the parts of the same weed taken as a whole.

RESUME OF BALCH'S WORK ON THE CHEMISTRY OF CERTAIN ALGAE ON THE PACIFIC COAST—PUBLISHED IN THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY, DEC., 1909.

In brief, Mr. Balch conducted his investigations as follows:

Comparative analyses were made of different species of weed which were collected at different stages of development. His analyses may be classified under these headings:

- (1) Effloresced salts which fell away from the entire weed during the course of drying.
- (2) Young weeds.
- (3) Mature weeds.
- (4) Stems.
- (5) Bladders.
- (6) Leaves.

A comparative summary of the work done by Balch and the work done by ourselves is shown in Table I. Inasmuch as this thesis is concerned with the potassium chloride and iodine content alone, we include these two constituents only in the comparative summary.

An inspection of the table will show that our analysis of the weed *Nereocystis Leutkeana* agrees fairly closely with that made by Balch, it being:

KCl	52.71%	vs. 55.10%
I	0.23%	vs. 0.24%

It would hardly be fair to compare our results on the second Pacific weed with those obtained by Balch, owing to the fact that our analyses are on the basis of the whole weed, while those of the former are upon the various parts of the weed.

It is at once evident that the investigations conducted by Balch and ourselves upon the Pacific weeds leave no room for doubt as to the superiority of these weeds over the sample obtained from the Atlantic.

Balch and ourselves agree closely upon the potassium chloride content of the crystallized salt obtained from the stems of the Pacific weed. Balch found double the amount of iodine that we determined in the same weed. Here it is evident that the iodine content of a weed is affected by the season of the year in which it was gathered and by its age, because we know that the samples in question were gathered at different seasons and it is safe to venture that they were not in the same stage of development.

A COMMERCIAL VIEWPOINT OF OUR RESULTS.

Our data shows that in a ton of the dry stems of the Pacific weed there is approximately a half-ton of potassium chloride whose purity is 80%. The present market value of this salt of a like purity is about \$42.00 per ton. A ton of the same weed contains four

pounds of iodine, the value of which is about \$2.00 per pound. This gives the stems the following value:

Potassium Chloride	\$21.00
Iodine	8.00
Total value	\$29.00

The analysis of the second Pacific weed, which represents the average contents of all the parts, shows that a ton of the dry material contains about 600 pounds potassium chloride of 80% purity. According to market reports this salt is worth about \$40.00 per ton. Upon this basis, a ton of the whole weed, i. e., all parts included, has the following value:

Potassium Chloride, 600 pounds.....	\$12.00
Iodine, 2 pounds.....	4.00
Total value.....	\$16.00

In our experiments we found the distillation products of all three weeds to be worthless.

While the stems of the Pacific weed represent a value of \$28.00 per ton, it must be remembered that it would be more costly to treat stems alone than it would to treat the entire weed. In order to get stems the entire weed must be gathered, and the market value of the salts obtained from a ton of dry weed is but half that of those obtained from a ton of dried stems.

Mr. Balch states that a ton of thoroughly air dried kelp should be worth about \$25.00. He also says that the volatile and non-volatile distillation products are valuable. He does not, however, tell what constituents are in the distillation products, neither does he show us where they could be marketed and what their value would be.

We find that a ton of the Pacific weed has but 60 per cent of the value estimated by Balch. This does not take account of the fact that he assigns a value to the distillation products while we do not. We know nothing as to the cost of gathering and treating this weed, but we do know that more must be paid for common labor in the Pacific States than in Chicago. Again, the market for the products manufactured from the weed is closer to New York than to the Pacific states. This would mean that a lower freight rate could be offered by New York jobbers who are selling the same products.

Balch states that the potassium chloride obtained by him has a purity high enough to meet the requirements of a chemically pure article. This was true only in the case of the effloresced salts which fell from the dried weed.

We believe that neither Balch nor ourselves possess sufficient data regarding markets and cost of production to justify us in saying that the treatment of Pacific weeds would be a commercial success. The species of Atlantic weed examined, owing to its low potassium content and lack of iodine, is not to be considered as a commercial proposition.

We are satisfied that to obtain any kind of a yield of iodine upon an experimental scale, would necessitate the treatment of a much larger amount of weed than was used in this investigation.

In conclusion we say that, while our results are not very promising, it would well be worth the while to further investigate the possibilities of the Pacific weed. By a further investigation we mean experimenting upon a more comprehensive scale. It is said that the solid portion of the stem, which grows down near the rocks, contains by far more iodine than any other part of the weed. It would be interesting to go out in a tug boat and find out what difficulties would be encountered in cutting this weed off close to the rocks, and what sort of a contrivance would be required for getting the harvested weed to shore. This data, supplemented by a more thoro investigation than our own, would give a good idea as to whether the weed might be treated for its potassium salts and iodine on a commercial scale.

The first shipments of Egyptian phosphate rock were received in Rotterdam last fall. On a minimum basis of 64 per cent tricalcium phosphate the material commanded a price of $10\frac{1}{2}$ cts. per unit c. i. f. London.

The total value of the exports of iron and steel from the United States has increased from \$103,000,000 in 1901 to nearly \$250,000,000 in 1911.

There has recently been a decline in metallic output of Oregon, and so far as present data show, this decline was more marked in 1911 than in 1910, according to Charles G. Yale, of the United States Geological Survey. The total number of active mines shows little change, but some of the larger ones have become less productive. Several gold dredges are in operation, but the most productive was not worked for several months in 1911. The hydraulic mines are the most productive placers, and their number is greatest. The deep mines of the state are yielding larger quantities of milling ore than formerly, but the grade of ore worked has declined nearly one-half. This accounts for the falling off in total gold production. Some siliceous ore is shipped to smelters, but most of it is milled, and comparatively little copper ore is now being smelted. The output of silver in the state is small. Baker County is still the largest producer of gold. It includes the districts of Baker, Cornucopia, Cracker Creek, and Mormon Basin, and between 50 and 60 producing mines, about half of which are placers, though much the larger proportion of the gold is obtained from deep mines. In gold output from placer mining Josephine County leads. There are 12 counties in the state now producing gold. In southwestern Oregon the placer mines are producing larger quantities than the deep mines; in northeastern Oregon the lode mines are much the most productive. According to preliminary figures prepared by the Director of the Mint, Oregon produced, in 1911, \$599,235 in gold and 69,116 fine ounces of silver, valued at \$38,014, against \$681,400 in gold and 43,800 ounces of silver, valued at \$23,600, in 1910.

NEW PHILIPPINE ESSENTIAL OILS.*

BENJAMIN T. BROOKS.

Ylang-ylang oil, extracted from *Canangium odoratum* (L.) Baill., is the only essential oil exported in large quantities from the Philippines. This paper contributes some information concerning certain new essential oils and several others, well known, which, until now, have not been reported from the Philippines.

The Essential Oil of Michelia Champaca L.—In experimenting with Champaca flowers it is essential to work rapidly, as after they have been picked a few hours they begin to turn brown and their fragrance is seriously impaired. This is due to the presence of an oxidizing ferment. However, the development of the color may take place slowly after the enzyme is killed or inhibited by certain poisons. An aqueous solution of the oxidase turns tincture of guaiacum blue directly and oxidizes certain phenols. The solution turns brown at the surface the instant it is exposed to the air, but previous heating for a few minutes to 100° will prevent the action.

The constants of two specimens of champaca oil recently prepared here are as follows:

Constants.	—Specimen No.—	
	1.	11.
Specific gravity $\frac{30^{\circ}}{30^{\circ}}$	0.904	0.9107
Refractive index N $\frac{30^{\circ}}{D}$	1.4640	1.4688
Ester number	124	146
Ester number after acetylating.....		199

The Oil of Michelia Longifolia BL.—Since champaca oils which were prepared from mixtures of the white and yellow flowers have been described, it was thought advisable to compare the oils from the two species.

The purified oil of longifolia was dark green in color and was not fluorescent either when pure or in alcoholic solution. It possessed an intensely sweet, almost nauseating odor, which is altogether unlike the odor of the oil from the yellow flowers. Its constants are: Specific gravity, 0.897; ester number, 180.0; refractive index N $\frac{30^{\circ}}{D}$, 1.4470.

The oil from white champaca blossoms contains linalool, methyl eugenol, methyl-ethyl acetic acid, probably in the form of methyl or ethyl ester, acetic acid probably as linalyl acetate, and a phenolic substance possessing an odor closely resembling thymol.

The oil from yellow champaca blossoms contains, in addition to isoreugenol, benzoic acid, benzyl alcohol, benzaldehyde, cineol and p-eresol methyl ether.

The Essential Oil of Clausena Anisum-olens (Blanco) Merr.—Sixteen kilos of leaves were distilled with steam for five hours, 185 grams of colorless oil being obtained. The oil resembled the fresh leaves in odor,

*Abstracted by B. B. Freud from the Philippine Journal of Science, Vol. vi., No. 4, Aug., 1911.

and possessed the following constants. Specific gravity $\frac{30^\circ}{30^\circ} = 0.963$; $N \frac{30^\circ}{D} = 1.5235$; saponification No. 3.6; the oil is inactive. Fractional distillation at atmospheric pressure of 90 grams of the oil gave the following results:

Temperature. °C.	Fraction. Grams.	Per Cent.
212-214	82.0	91.1
214-216	4.5	5.0
216-222	2.5	2.7
Residue	1.0	1.1

The oil has a paint odor of anise or anethol, which, together with the constants, identifies it almost with certainty as methyl chavicol, which is present to the extent of about 93 per cent. The total yield of the essential oil is about 1.20 per cent.

Philippine Citrus Oils.—Several varieties of citrus fruits are widely grown in the Philippines, yet no attempt has been made to secure essential oils from them on a commercial scale. The present production of fruit is immediately consumed in the local markets. However, any considerable increase in the number of trees planted would at once bring the manufacture of citrus oils within the range of possibility. The variety of orange now most widely cultivated, the *naranjita*, contains very little acid and, in the opinion of the author, could not be used for making citrus acid. In Italy, where practically the world's supply of orange oil is produced, the citric acid which is manufactured from the juice, has a value about equal to the oil obtained from the peel.

Fine, large lemons, grown from the seed of Italian lemons, are raised in one or two localities in the mountains of Northern Luzon, but, so far, no attempt at extensive cultivation has been made. Therefore, true lemon oil can not be produced in the Philippines at the present time, or in the immediate future.

Orange peel oil can be prepared from the two varieties, *naranjita* and *cajel*. The peel of the former contains much more oil than the latter, and also probably more than the average California orange. The yield is greater when the peels are green than when they are fully ripe.

The green oranges weigh, on an average, about 160 grams, of which about 40 grams are peel. On an average the peel of a green orange yields, on squeezing by hand, about 0.5 gram of oil and 2 cubic centimeters of an aqueous solution which contains a considerable amount of reducing sugars. No evidence of the presence of a glucoside was found. The freshly pressed oil has the following constants: Ester number, 8.0;

optical rotation, $A \frac{30^\circ}{D} = 90.85^\circ$; refractive index,

$N \frac{30^\circ}{D} = 1.4700$. The oil in question appears to be

identical with the orange-peel oil of commerce.

The odor of the Philippine oil is just as fine as the oil produced elsewhere, being decidedly sweeter than several samples of Sicilian oil procured in Manila. However, the latter samples undoubtedly had deteriorated during storage.

The Essential Oil of Citrus Decumana Murr.—The oil in the peel of the fruit of this species, which is commonly known to Americans as grapefruit or pomelo, is very difficult to express and appears to have no extraordinary merit. The oil from the leaves has never been described. The leaves are extremely fragrant and on distillation with steam yield about 1.7 per cent of an oil having a very fine odor. The constants of a sample prepared in this way were as follows:

Specific gravity, $\frac{30^\circ}{30^\circ} = 0.8700$; ester number 10;
optical rotation, $A \frac{30^\circ}{D} = 22.90^\circ$ refractive index, $N \frac{30^\circ}{D}$

1.4644. It is miscible with 70 per cent alcohol.

It appears that there are two varieties of pomelo trees. It has been noted that one variety has large leaves with almost no oil; the other has a much smaller leaf and the branches are quite thorny. The small leaves are full of oil cells and give the yield on distillation noted above.

The oil contains less than 1 per cent of aldehydes. Treatment of 40 grams of oil with sodium acid sulphite, in the cold, and subsequent treatment of the sulphite solution, gave one or two drops only of an oil having an odor like citral. Thirty-nine grams of the oil were recovered.

Dipentene constitutes about 25 per cent of the oil, as was shown by isolating a fraction boiling from

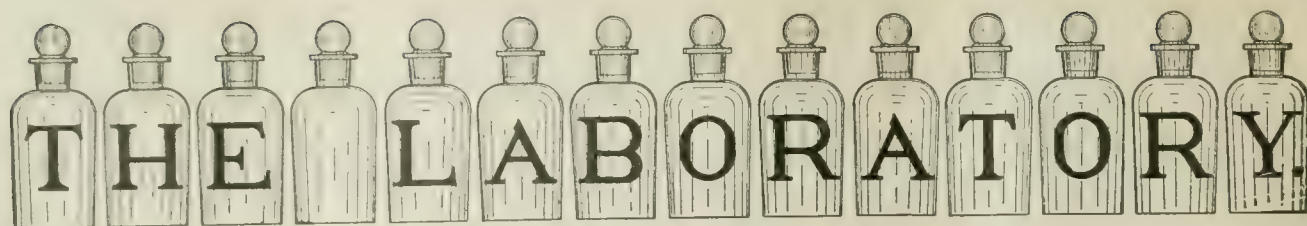
$174^\circ-176^\circ$. $A \frac{30^\circ}{D} = +2.35$; $N \frac{30^\circ}{D} = 1.4750$ and spe-

cific gravity $\frac{30^\circ}{30^\circ} = 0.8181$, which gave dipentene te-

trabromide, melting point 120° . The fraction boiling from 195° to 200° , 15 per cent of the oil, contains linalool, as was shown by oxidizing to citral by chromic acid mixture.

Citrus Hystrix, DC.—The oil of *Citrus Hystrix* DC. is referred to by Schimmel & Company as having an odor somewhat resembling that of bergamot. The oil distilled here from the leaves possesses an odor very much resembling that distilled from the leaves of the pomelo, *Citrus decumana* Murr. It is very fragrant, but the yield is so poor, not more than 0.08 per cent, that a quantity sufficient for investigation was not distilled. The constants of the oil are as follows: Specific

gravity, $\frac{30^\circ}{30^\circ} = 0.9150$; $N \frac{30^\circ}{D} = 1.4650$; $A \frac{30^\circ}{D} = 10.50^\circ$; saponification number, 50.2.



THE QUANTITATIVE SEPARATION OF MIXTURES OF CERTAIN ACID COAL TAR DYES.

The use of immiscible solvents for separating mixtures of acid coal tar colors is discussed in most standard works on the subject. Loomis¹ gives data concerning the solubility of a large number of common dyes, and Seeker² has published qualitative separations of Orange I and Naphthol Yellow S from certain other dyes depending on the use of amyl alcohol. In such procedures any variation made in the acidity has been attained by using acids of different degrees of dissociation, as acetic acid and a mineral acid, and not by adding varying amounts of the same acid. Chiefly with the object of making a quantitative separation of the colors permitted in foods (Naphthol Yellow S, Ponceau 3 R, Orange I, Amaranth, Light Green S F Yellowish, Erythrosin and Indigo Carmin),³ their ratios of distribution between dilute hydrochloric acid of different concentrations and certain immiscible solvents were determined.⁴ The data indicated a method that gives good results in practice and is of quite general applicability. Some figures have also been obtained for other similar colors that will show where separations can be made and can also be applied for qualitative differentiations. These data are set forth in a circular issued recently by the Bureau of Chemistry of the U. S. Department of Agriculture. This circular was prepared by W. E. Mathewson of the New York Food and Drug Inspection Laboratory and is of such practical interest that we are reprinting it in full.

DATA OBTAINED.

In Table I the figures given show the percentage of color remaining in the aqueous layer after shaking with an equal volume of the immiscible solvent. A solution containing a quantity of dye equivalent to 0.1000 gram of pure color was diluted to 50 cc with water and standardized hydrochloric acid, sufficient of the latter being taken to give the solution exactly the acid normality desired. It was then shaken out with 50 cc of the solvent. (This shaking was continued for five minutes with dichlorhydrin, two minutes with the other solvents.) After separation of the liquids, which

takes place very rapidly with strongly acid mixtures but more slowly with low acid concentrations, the lower layer was drawn off and the percentage of dye remaining in the water layer estimated. All color determinations were made by Knecht and Hibbert's method,⁵ a standard solution of pure amaranth being used to titrate back any excess of titanium chlorid added. The extractions were made at room temperature, 27° to 30° C.

Of the coloring matters used, the permitted food colors were from analyzed commercial samples of excellent grade. The others were commercial samples of good quality, their examination, however, being limited in most cases to a determination of total color and a comparison of their reactions with the description given in Heumann and in Schultz and Julius (translated and enlarged by A. G. Green, 1904). The serial numbers used in the latter work are given with the names of the dyes.

DISCUSSION OF RESULTS.

In applying the data given in the table for effecting the quantitative separation of two colors the following procedure, or some simple modification of it, has been practiced. The solution containing 0.2 to 0.4 gram of color (depending on the nature of the dyes) is treated with sufficient water and hydrochloric acid of known strength to bring its volume to about 50 cc and its acid concentration to that point for which the difference in percentage of color extracted for the two dyes is near its maximum. The solution is then shaken out with the immiscible solvent, being passed in succession through three or four separatory funnels each containing 50 cc of the latter. The portions of the solvent are washed with 50 cc of hydrochloric acid of the same normality as the solution, being passed successively through the separatory funnels in the same order as was the original solution, and this operation is repeated with one or two fresh amounts of the hydrochloric acid. The dye relatively more soluble in water is determined in the combined washings and extracted solution. The second dye is removed from the solvent by shaking with water, very dilute caustic soda, or, more quickly, with dilute caustic soda after the addition of some gasoline, or similar substance in which the color insoluble.

Assuming the distribution ratios to remain constant, this procedure using four funnels and making three washings gives for a pair of colors whose "distribution

¹U. S. Dept. Agr., Bureau of Chemistry Cir. 63.

²Allen's Commercial Organic Analysis 4th ed., vol. 5.

³U. S. Dept. Agr., Office of the Secretary, Food Inspection Decision 76.

⁴Distribution ratios of the permitted dyes between dilute hydrochloric acid and amyl alcohol were sent out by the writer in April, 1911, in a circular letter in connection with the co-operative work of the Association of Official Agricultural Chemists.

⁵New Reduction Methods in Volumetric Analysis, 1910.

⁶Color acid nearly insoluble in both layers.

⁷Similar to Congo Red but color acid more soluble in alcohol.

numbers" (as the percentage numbers given in the table may be called) are 80 and 20, respectively, a separation of 98.30 per cent for each color. With distribution numbers 90 and 10 four funnels and three washings give a calculated separation of 99.73 per cent, and the same is obtained with distribution numbers 81.8 and 5.3 if the solvent in which the dyes are relatively more soluble be taken in portions one-half the volume of those of the other liquid. If the second, third and fourth funnels be given a fifth washing, the third and

lied to take place. With amyl alcohol as solvent it is almost always desirable to make the original solution more strongly acid than is indicated by the distribution data and use relatively more portions of the washing liquid.

Of the permitted colors, Naphthol Yellow S is best separated from Orange I by washing the amyl alcohol solution of the color acids with strong salt solution, care being taken that not too much color is present. With a solution containing 20 grams of salt and 0.04 gram Naphthol Yellow S per 100 cc and shaken with an equal volume amyl alcohol, 97 per cent of the color is retained by the water. With a similar solution containing 0.07 gram Orange I, the water layer contains 1.5 per cent of the total color. With higher concentrations some color may be salted out in solid form, but this does not interfere if the amount is small. Erythrosin being quantitatively removed from slightly acid solutions by amyl acetate, ether, or amyl alcohol, its separation from sulphonated colors presents no difficulty.

ANALYSES OF MIXTURES.

Analyses of a number of mixtures were made with the following results. In all cases the last washings were free or practically free from colors. As the determination of total color is convenient and accurate, it was in most cases made together with that of the dye reacting with the lesser amount of titanium trichlorid.

Naphthol Yellow S and Light Green S F Yellowish.—Twenty cc of a solution containing in this volume 0.1000 gram Green, and 0.1083 gram Yellow was treated with 20 cc five-normal hydrochloric acid and diluted to 50 cc, then shaken out with three portions of amyl alcohol of 50 cc each. The amyl alcohol was washed with two portions (50 cc each) of two-normal hydrochloric acid. Green was determined in the extracted solution and washings, total color in another aliquot of the original solution.

Green, found 0.0975 gram = 97.5 per cent.

Yellow, found 0.1085 gram = 100 per cent.

Naphthol Yellow S, Orange I and Indigo Carmin.—Thirty cc of solution containing 0.1000 gram Orange, 0.1000 gram Blue, and 0.1083 gram Yellow was treated with 2 cc five-normal hydrochloric acid and shaken through three funnels containing each 60 cc amyl alcohol. The latter was then washed with two portions of dilute hydrochloric acid (2 cc five-normal hydrochloric acid + 28 cc water, or one-third normal). The second and third funnels were then washed with a third portion of acid (30 cc) and the third funnel with a fourth portion. The Blue was determined directly in the extracted solution and washings.

The amyl alcohol was then washed with four portions of 120 cc each sodium chlorid solution (200 grams per liter). The second and third funnels were washed a fifth time and the third a sixth time.

Blue, found 0.099 gram = 99 per cent.

Orange, found 0.0985 gram = 98.5 per cent.

TABLE I.—PERCENTAGE OF COLOR IN THE WATER SOLUTION AFTER SHAKING WITH AN EQUAL VOLUME OF IMMISCIBLE SOLVENT.

Colors.	Normality of hydrochloric acid in water layer before shaking—							
	Percentage of color in water solution after shaking.							
	4	2	1	½	¼	⅛	1/16	1/32
Naphthol Yellow S No. 4 ..	..	4	7	11	17	27	43	
Orange I No. 85.....	..	..	..	0.5	1	2	4	
Ponceau 3 R No. 56.....	..	1	3	7	21	43	64	78
Amaranth No. 107.....	5	15	52	82	93	..	..	..
Light Green S F No. 435	90	95	97	99	99	..	..	..
Erythrosin No. 517.....	..	..	..	..	..	..	..	0.0
Indigo Carmin No. 692..	34	51	89	96	99	..	..	..
Fast Yellow No. 8.....	36	..	61	..	..	..	..	..
Grocein Orange G No. 13	..	..	..	..	..	1	2	..
Orange G No. 14.....	..	..	18	..	58	..	..	..
Ponceau 2 R No. 55.....	2	..	14	..	..	..	..	..
Crystal Ponceau No. 64	..	..	..	8	..	39	..	..
Fast Red B No. 65.....	..	2	..	16	..	62	..	..
Resorcin Yellow No. 4..	..	..	..	5	..	11	17	..
Orange II No. 86.....	..	..	..	..	..	2	3	..
Brilliant Yellow S No. 89	..	73	..	90	..	..	..	..
Tartrazin No. 94.....	..	47	..	88	..	..	..	..
Metanil Yellow No. 95..	..	..	..	..	1	1	..	..
Fast Red A No. 102.....	..	..	..	..	0.2	1	..	..
Fast Red C No. 103.....	..	1	..	4	..	..	..	..
Fast Red E No. 105.....	..	1	..	17	..	68	..	..
New Coccin No. 106.....	15	..	..	75	..	..	..	..
Scarlet 6 R No. 108....	41	80	95	..	..	..	..	..
Resorcin Brown No. 137	..	..	..	8	..	20	..	..
Cotton Scarlet 3 B No. 146	..	..	..	2	..	10	..	..
Congo Red No. 240 ⁶	..	..	..	..	..	..	..	..
Azo Blue No. 287.....	..	..	..	..	..	..	..	..
Chrysophenin No. 329..	..	..	..	..	1	2	..	..
Guinea Green B No. 433	..	..	48	..	32	25	..	..
Acid Magenta No. 462..	75	..	93	..	..	..	..	..
Solvent: Dichlorhydrin.								
Naphthol Yellow S No. 4	..	15	..	..	..	..	..	..
Ponceau 3 R No. 56.....	..	37	..	..	..	..	..	..
Orange I No. 85.....	..	4	..	..	..	..	..	..
Amaranth No. 107.....	..	95	..	..	..	..	..	..
Light Green S F No. 435	..	15	..	17	..	..	..	..
Indigo Carmin No. 692..	..	91	..	..	..	..	..	..
Acid Magenta No. 462..	..	86	..	..	..	..	..	..
Solvent: Amyl Acetate.								
Naphthol Yellow S No. 4	22	33	48	..	..	..	..	..
Ponceau 3 R No. 56.....	95	96	97	..	..	..	..	..
Solvent: Ether.								
Naphthol Yellow S No. 4	..	94	97	..	..	..	..	..
Orange I No. 86.....	..	97	97	..	..	..	..	..

fourth funnels a sixth, and the last funnel a seventh washing, the calculated loss for the color more soluble in the solvent layer is 0.76 per cent, while the percentage of the other dye removed is relatively much increased (to 99.99 per cent). In most mixtures the progress of the separation is always apparent.

In practice, because of incomplete extraction and separation, and especially on account of uncertainty due to small amounts of subsidiary dyes always present, it is necessary to increase the number of successive extractions. The formation of esters of the color acids is a possible source of difficulty, but is not be-

Total color was determined and Yellow estimated by difference.

Yellow, found 0.1080 gram = 99.5 per cent.

Ponceau c R and Naphthol Yellow S.—Twenty cc of solution containing 0.1083 gram Yellow and 0.1168 gram Ponceau was treated with 20 cc concentrated hydrochloric acid and passed through four funnels containing each 60 cc of amyl acetate. The amyl acetate portions were washed with 3 portions of 30 cc each of four-normal hydrochloric acid, a fourth washing given to the last three funnels, a fifth to the last two, and a sixth to the last one. The amyl acetate solution was diluted with gasoline, the Ponceau removed by washing with very dilute caustic soda and determined in this solution. Total color was determined and Yellow estimated by difference.

Ponceau, found 0.1132 gram = 97 per cent.

Yellow, found 0.1089 gram = 100.5 per cent.

Amaranth and Orange I.—Twenty cc of solution containing in this volume 0.1000 gram Orange and 0.1723 gram Amaranth was treated with 2 cc five-normal hydrochloric acid and 28 cc water and passed through two funnels containing 50 cc each of amyl alcohol. The latter were then washed twice with 50 cc volumes of eighth-normal hydrochloric acid. Amaranth was determined directly in the extracted solution and washings. Total color was determined in an aliquot of the original solution.

Amaranth, found 0.1731 gram = 100.5 per cent.

Orange, found 0.0995 gram = 95.5 per cent.

Light Green S F Yellowish, Amaranth, Ponceau 3 R, and Orange I.—Thirty-seven cc solution containing in this volume 0.1000 gram Green, 0.1000 gram Ponceau, 0.1000 gram Orange, and 0.1162 gram Amaranth was treated with 20 cc of concentrated hydrochloric acid and shaken through three funnels containing each 50 cc amyl alcohol. The latter was washed with three portions (50 cc) of four-normal hydrochloric acid. Green was determined in the extracted solution and washings.

Two more funnels containing 50 cc portions of amyl alcohol were now added and the series washed with five 50 cc amounts of fourth-normal hydrochloric acid. The first washing was colorless on coming from the fourth funnel and was discarded. The second, third, fourth and fifth funnels were given a sixth additional washing, the last three a seventh, the last two an eighth, and the last one a ninth. The extracted solution and washings were combined, nearly neutralized with two-normal ammonium hydroxid, evaporated to about 150 cc, and Amaranth determined.

A second portion of 37 cc of the original solution was treated with 2 cc of five-normal hydrochloric acid and made up to 75 cc, then shaken out with four 25 cc portions of amyl alcohol. These were washed with five portions (75 cc each) sixteenth-normal hydrochloric acid. The last three funnels were given a sixth washing, the last two a seventh, and the last one an

eighth. The amyl alcohol was then diluted with gasoline, the Orange removed with dilute caustic soda and estimated. Total color was determined in an aliquot of the original solution and the Ponceau found by difference.

Green, found 0.098 gram = 98 per cent.

Amaranth, found 0.116 gram = 100 per cent.

Orange, found 0.102 gram = 102 per cent.

Ponceau, found 0.098 gram = 98 per cent.

Ponceau 3 R and Indigo Carmin.—Twenty-eight cc of solution containing 0.1000 gram Ponceau and 0.1000 gram Blue was treated with 2 cc five-normal hydrochloric acid and shaken with four 50 cc portions of amyl alcohol. Three portions (50 cc each) of third-normal hydrochloric acid were then passed through the series of funnels, a fourth washing given to the last three, a fifth to the last two, and a sixth to the last one. Blue was determined directly in the extracted solution and washings. Total color was estimated and the Ponceau obtained by difference.

Blue, found 0.102 gram = 102 per cent.

Ponceau, found 0.099 gram = 99 per cent.

Light Green S F Yellowish and Indigo Carmin.—Twenty-three cc solution containing 0.1000 gram Blue and 0.1000 gram Green was treated with 2 cc five-normal hydrochloric acid and shaken out with six 25 cc portions of dichlorhydrin (saturated with water). The dichlorhydrin portions were passed successively through four funnels containing each 25 cc of fourth-normal hydrochloric acid saturated with dichlorhydrin. They were then combined, diluted with benzol, the color removed with water, and titrated. Total color was determined and Blue found by difference.

Green, found 0.099 gram = 99 per cent.

Blue, found 0.101 gram = 101 per cent.

Naphthol Yellow S and Amaranth.—A 10 cc solution containing 0.1273 gram Amaranth and 0.1083 gram Yellow was treated with an equal volume of concentrated hydrochloric acid and shaken through three funnels containing each 40 cc amyl acetate. The amyl acetate portions were then washed with 20 cc of six-normal hydrochloric acid and the last two funnels given a second washing. The Amaranth was determined in the extracted solution and washings. The Naphthol Yellow S was removed from the amyl acetate by washing with a little dilute caustic soda solution and determined directly.⁸

Amaranth, found 0.128 gram = 101 per cent.

Yellow, found 0.108 gram = 100 per cent.

In using the table to distinguish qualitatively between such colors as Amaranth and the other Fast Reds, or Guinea Green and Light Green S F Yellowish, it must be remembered that the relative intensity of the coloration of the two layers is usually somewhat different from their relative concentration and may be very much so.

⁸Naphthol Yellow S is conveniently titrated in tartrate solution, a little Light Green S F Yellowish being added to serve as indicator.

QUALITATIVE REACTIONS OF VEGETABLE TANNINS.*

By EDMUND STIASNY and C. D. WILKINSON.

The last Conference of the I. A. L. T. C. in Paris, September, 1910, has decided that the behavior of vegetable tannins against different reagents should be studied by a commission. The following report of our experimental results may be regarded as a first step in this work, and it is published here mainly for the purpose, that our suggestions may be examined by as many colleagues as possible, and that the collected report of a large number of tests carried out by different workers may prove valuable for our knowledge on vegetable tannins.

The goal which we must finally try to reach is, identify a single tannin material in the form of its extract or liquor, to prove decidedly if any extract is pure or not, and to determine the components in any mixtures of vegetable tannin solutions.

Any work in this direction has to be based on our present knowledge of the qualitative behavior of tannins, starting with the examination of these known tests and trying to modify and elaborate them to increase their value. Procter's "Laboratory Book" is the best guide for this part of the work, and we have made use of it in many respects. Another part of our work deals with attempts to find new methods for distinguishing different vegetable tannins. Here we hope to give some valuable suggestions, as well as to state some negative results, in order to prevent other colleagues from wasting time with similar experiments.

No color tests have been used, because they are liable to individual errors, and principally because they do not work in the case of mixtures. We thought that those tests were the more important ones, which allow a separation of different tannins; we therefore studied mostly precipitation tests as to the formation, completeness and solubility of the precipitate formed. As a preliminary scheme the following tests and conditions were chosen: The tannin solution was made of three different concentrations, viz., analytical strength (3.5—4.5 gram tannin per liter), one-tenth of this strength, and 6—8 times the same. The observations were made immediately, and when required repeatedly during the first hours, and in all cases after allowing them to stand over night. The reagents were always used in the concentration given below and added to the tan solutions by means of pipettes, so that the most possible conformity may be obtained by different workers.

In this way, 34 different tannin solutions¹ were tested with sodium chloride, ammonium chloride, ammon-acetate, tartar emetic, lead acetate, bromine, copper sulphate and ammonia; ammonium sulphide, and formaldehyde. The results allowed us to eliminate

those tests which did not prove to be of value (precipitating with saturated solutions of sodium chloride, and ammonium chloride, and testing with ammonium sulphide)² and to choose the most suitable tannin concentrations for the other promising tests. It would take up too much space to give these preliminary results in table form and we may at once shortly report on the promising tests and their application for distinguishing some tannins in mixtures.

A. THE LEAD ACETATE TEST.

Completeness of the Lead Acetate Precipitation—All tannins are completely precipitated in as far as the filtrate from this precipitate gives in no case the iron-test (adding about 1 cc. iron alum solution (1 per cent.) to about 5 cc. of the filtrate). Valonia (2)³ mimosa (2), mangrove (2), oakwood, chestnut (3), myrobalans (4), algarobilla, divi-divi and gallotannic acid give no coloration, if excess of NaOH is added (to redissolve $Pb(OH)_2$) to the filtrate of the lead acetate-precipitate. But quebracho (6 extracts and a pure sample of wood) gives a yellowish color, the intensity of which increases with standing; the same is the case with ulmo, and most distinct with sumach (3 extracts and several samples of pure Sicilian sumach) and pistacia.

As to quebracho, the observation may be made that after shaking out the aqueous solution with ethylacetate, the remaining aqueous layer when precipitated with lead acetate gives a filtrate which remains colorless after addition of NaOH.

Basic lead acetate leads in all cases to a filtrate which remains colorless after adding excess of NaOH.

Some samples of wood pulp (4) are not, others only very incompletely, precipitated with lead acetate and a little more but still always incompletely with basic lead acetate, the filtrate being yellow and giving distinctly deeper color with NaOH.

Solubility of the Lead Precipitate in Acetic Acid.—Quebracho (3), mangrove (2), ulmo, mimosa (2), gambier gave a lead precipitate which was entirely soluble in acetic acid. The test was made by adding 10 cc. acetic acid (10 per cent.) to the mixture of 5 cc. tannin solution and 5 cc. lead acetate (10 per cent.); or, preferably, by first adding 10 cc. acetic acid to 5 cc. of the tannin solution, and then adding 5 cc. of the lead acetate. In the latter case no precipitate is produced with catechol tans, provided they have not been sulphited (3). Then of course some lead sulphate is formed and small amounts of tannin are carried down by this precipitate. The behavior of pistacia is stated later on.

Pyrogallol tans differ from the behavior of catechol tans, their lead precipitated being insoluble or but partially soluble in acetic acid. Insolubility was observed in the case of oakwood, chestnut (some samples showed a small solubility) and valonia, partial solu-

*From the Journal of the Leather Chemists' Association.

¹All tanning materials and extracts used in this paper are guaranteed pure materials, kindly sent for our use by several tannin extract works in England and the Continent.

²The Eitner-Philp test will be dealt with below.

³These figures in brackets mean the number of samples of different extracts which have been tested.

bility in the case of sumach, myrobalans, divi-divi, algarobilla and gallotannic acid.

Table I shows the behavior of catechol and pyrogallol tans, of wood pulp and some mixtures.

Some remarks may be added to Table I. Mimosa, it is known (see Procter's Laboratory Book, p. 161), behaves differently towards ferric salts than the other catechol tans; this is also observed in the filtrate of the acetic acid lead acetate precipitation, which turns violet and not green after adding the ferric salt. The green color produced in the filtrates of the other catechol tans is best observed during the addition of iron alum (added from a dropping bottle). Subsequent addition of solid sodium acetate turns this green color

only. But unfortunately the delicacy of the test with basic lead acetate is much less than that with lead sugar, and smaller amounts of wood pulp easily escape observation. The lead acetate test may be considered valuable in the case of determining wood pulp in chestnut extracts. If the formaldehyde test shows absence of any precipitate during testing and the lead acetate test gives yellow coloration, then the presence of wood pulp is proved.

In all cases, however, it is advisable to apply Procter and Hirst's aniline test to confirm the result. (See *Collegium*, 1909, p. 185.)

(b) Detection of catechol tans in mixtures with oakwood, chestnut and valonia extracts, 5 cc. tannin

TABLE I.
5 c.c. tannin solution (analytical strength) + 10 c.c. acetic acid (10 per cent) and 5 c.c. lead acetate (10 per cent).
Reaction of the filtrate.

Catechol tans.	+Iron alum.	+Iron alum. +Sodium acetate.
Quebracho no pp.....	Olive-green	Violet.
Quebracho sulf. very slight pp.....	Green	Violet.
Mangrove no pp.....	Olive-green	Violet.
Ulmo no pp.....	Green	Violet.
Gambier no pp.....	Green	Deep green, the lower layer clear blue.
Mimosa no pp.....	Deep bluish violet.....	Deep bluish violet.
Pistacia pp.....	Both green and violet.....	Both dirty green and violet.
Wood pulp no pp.....	No distinct coloration.....	No distinct coloration.
Pyrogallol tans.		
Chestnut pp.....	Faint bluish violet.....	Violet.
Oakwood pp.....	No distinct coloration.....	No distinct coloration.
Valonia pp.....	No distinct coloration.....	No distinct coloration.
Sumach pp.....	Violet	Violet.
Divi-divi pp.....	Violet	Violet.
Algarobilla pp.....	Violet	Violet.
Myrobalans pp.....	Deep bluish violet.....	Deep bluish violet.
Gallotannic acid pp.....	Deep bluish violet.....	Deep bluish violet.
Mixtures.		
Oakwood and quebracho (20%) pp.....	Faint green	Faint violet.
Chestnut and quebracho (20%) pp.....	Faint dirty green.....	Violet.
Valonia and quebracho (20%) pp.....	Green	Violet.
Chestnut and myrob's (20%) pp.....	Violet	Violet.
Oakwood and myrob's (20%) pp.....	Faint violet.....	Violet.
Valonia and myrob's (20%) pp.....	Faint violet.....	Violet.

into a distinct violet; only gambier remains green, the shade being intensified by the sodium acetate, and the lower layer near the solid salt appearing bright blue. In the case of pistacia, a copious precipitation is obtained with acetic acid and lead acetate, and in the filtrate both the green and the violet coloration can be distinctly seen after adding the iron salt, showing the pistacia contains a mixture of different tans.

Application of the Lead Acetate Test for the Detection of Mixtures.—(a) A test for wood pulp extract suggests itself by the different behavior of wood pulp and tanning liquors towards lead acetate. To 5 cc. tannin solution (analytical strength) 5 cc. lead acetate (10 per cent.) are added, and a portion of the clear filtrate is mixed with an excess of NaOH (10-20 per cent.) (the NaOH solution ought to be fairly fresh); if the filtrate remains colorless, no wood pulp is present; 10-20 per cent. wood pulp extract will give distinct yellow color, but a slight yellow coloration may also be due to the presence of quebracho, sumach and pistacia; in this case the test must be repeated with basic lead acetate, when a yellow coloration of the filtrate by addition of NaOH will be due to wood pulp

solution (analytical strength) + 10 cc. lead acetate (10 per cent.), mixed, filtered, and some drops of iron alum (1 per cent.) added to the filtrate. If a green color appears, which is best observed during the addition of the iron salt from a dropping bottle, the presence of catechol tans is proved. This test, however, is not very delicate, showing scarcely less than 10-15 per cent. of the catechol tan, and requiring some practice in its use. (See table I, mixtures.)

(c) Even the presence of myrobalans in oakwood, chestnut or valonia can be observed with some degree of reliability by the acetic acid lead acetate test, the filtrates of the precipitates of pure oakwood, chestnut or valonia remaining colorless (or nearly colorless with iron alum while the presence of myrobalans (as well as that divi-divi, algarobilla, and sumach) produces a distinct violet tint. (See table I, mixtures.)

B. THE TARTAR EMETIC TEST.

1. Five cc. tannin solution (analytical strength) + 10 cc. tartar emetic (4 per cent.). Quebracho (6), mangrove (2), and ulmo gave no precipitate (in some

*One mimosa sample gave precipitate only after standing over night.

cases the solution after 24 hours turned turbid); gambier became turbid; chestnut (3), mimosa (2),⁴ myrobalans (4), sumach (3), valonia (2), pistacia, divi-divi, and algarobilla gave more or less incomplete precipitates. The filtrate of these precipitates gave green color with iron alum; this is—in the case of pyrogallol tans—due to the presence of tartaric acid. One sample of oakwood was completely precipitated, the filtrate not answering to the iron test. Wood pulp solution is not precipitated by tartar emetic.

It may be specially mentioned that mimosa behaves like a pyrogallol tan in this test; we shall see later on that such behavior of mimosa is met with in several other reactions.

2. Five cc. tannin solution (analytical strength) + 10 cc. of a mixture of tartar emetic (4 per cent.) and sodium chloride (4 per cent.).

All tannins were precipitated, but only in the case

solutions.⁵ Two or three cc. tannin solution (0.1 analytical strength) + 3 — 5 drops copper sulphate (1 per cent.) + about 3 cc. NH_3 (5 per cent. NH_3).

Quebracho (6), mangrove (2), ulmo, gambier, pistacia give no precipitate. Chestnut, oakwood, sumach give immediately precipitate, mimosa gave precipitate after standing over night; three of the myrobalan extracts which we investigated gave no precipitate, one gave a precipitate after standing over night; algarobilla and divi-divi gave slight precipitates after standing for some time; wood pulp gives no precipitate.

E. THE EITNER-PHILIP TEST.

Twenty-five cc. tannin solution (6 times analytical strength) + 2-3 drops concentrated sulphuric acid (in case of sulphited extracts take 4-5 drops; excess of acid must be avoided in order to prevent separation of sulphur on the subsequent addition of ammonium sulphide); boil one to two minutes, cool down, add about

TABLE II.

	Behavior during 10-15 min. boiling	Color of filtrate colorless	Reaction of the filtrate	
			+ iron alum + sodium acetate not blue	+ NaOH
Quebracho (7)	pp	"	"	slightly yellow
Mangrove (3)	pp	"	"	color increasing
Ulmo	pp	"	"	by standing
Mimosa	pp	"	"	colorless
Gambier	pp	"	"	slightly yellow
Pistacia	pp	"	"	reddish brown
Oakwood	clear	slightly colored	blue	"
Chestnut (3)	clear	"	"	"
Myrobalans (4)	clear to turbid	"	"	"
Valonia (2)	clear to turbid	"	"	"
Sumach (3)	gradual pp	distinctly	"	"
Divi-divi	clear to turbid	strongly	"	yellow to red to
Algarobilla	{ clear to } { slightly turbid }	"	"	{ yellow (again) red
Wood pulp (4)	clear	dark	not blue	very dark

of oakwood, the precipitation was complete. Wood pulp is not precipitated by this test.

C. THE AMMON-ACETATE TEST.

This test is best carried out with strong tannin solutions.

Five cc. tannin solution (6-8 times analytical strength) + 10 cc. ammon-acetate (40 per cent.). All catechol tans (quebracho (6), mangrove (2), ulmo, mimosa (2), gambier, and pistacia) give no precipitate. On the contrary they often become clearer than before. If alumina salts are present, even in very small amounts, a copious precipitate appears. Chestnut and oakwood give immediately copious precipitate. Valonia, myrobalans, algarobilla and divi-divi are gradually precipitated, while in the case of sumach a precipitate could only be observed after standing for hours (over night). Wood pulp alone gives no precipitate, but mixtures of wood pulp with any tannin give immediately copious precipitate.

Application of the Ammon-Acetate Test.—As a negative test for wood pulp in mixture with catechol tans. If no precipitate appears, wood pulp is absent.

D. THE COPPER SULPHATE-AMMONIA TEST (See *Procedure*, Laboratory Book, p. 150).

This test is best carried out in very dilute tannin

5 grams sodium chloride, mix and allow to stand for 5-10 minutes, filter and make the following test with the filtrate: Take 15 cc. of water in a test-tube, add 10-15 drops of yellow ammonium sulphide and 2-3 cc. of the filtrate, and note the appearance of a precipitate.

Quebracho (6), mangrove (2), ulmo, gambier, gave no precipitate. Mimosa, chestnut, oakwood, myrobalans (4), sumach (3), divi-divi, algarobilla and pistacia give precipitate. Some wood pulp extracts gave a precipitate, others did not.

Our observations agree entirely with those of Philip (*Coll.*, 1900, p. 240); mimosa behaves here also like a pyrogallol tan; the same may be said of pistacia.

F. THE FORMALDEHYDE.

Fifty cc. tannin solution (analytical strength) + 5 cc. strong hydrochloric acid + 10 cc. Formaldehyde (40 per cent.)⁶ boiled with reflux condenser for half an hour, cooled down very well and filtered. The appearance of a precipitate whilst boiling has to be looked for, and the filtrate is used for the following two tests:

⁵Oakwood, chestnut, myrobalans, mimosa gave no precipitate in solutions of analytical strength or in still stronger solutions, but they gave positive tests in 0.1 analytical strength.

⁶We took usually 50 cc. of the tanning liquor and added 25 cc. of a solution containing 100 cc. strong HCl, 100 cc. water and 150 cc. Formaldehyde (40%).

(A) Put about 10 cc. of the filtrate in a test-tube and add about 1 cc. iron alum (1 per cent) + about 5 grams, sodium acetate (solid) (not shaking); observe if blue (or violet) color appears in the lower layer.

(B) About 5 cc. filtrate + excess of NaOH (made alkaline); observe if coloration appears.

Table II contains the results obtained by the above tests; similar observations have been published by one of us in *Der Gerber*, 1905.

This table shows, that catechol tans are completely precipitated in as far as no iron test is given by the filtrate; but only in the case of mimosa no coloration was produced with excess of NaOH; this of course makes it impossible to suggest a method of detecting wood pulp in mixtures with catechol tans (only in mixtures with mimosa this test could have such application). Pistacia does not behave as a pure catechol tan according to the formaldehyde test.

No pyrogallol tan is completely precipitated, most of them giving no or only very slight precipitate; sumach gives by far the most precipitate, especially after cooling, so that the difference between sumach and pistacia is very small indeed as far as the formaldehyde is concerned.

The iron test is the most useful for testing the filtrate of those precipitates, especially if a mixture of catechol or pyrogallol tans is given, in which case amounts of 5 per cent. pyrogallol tan (and even less) can be detected with accuracy. The frequent adulteration of catechol tannin extracts with myrobalans can thus very easily be found. Wood pulp behaves like pyrogallol tans but no iron test is given.

G. THE BROMINE TEST. (See Procter, Laboratory Book, p. 149.)

Two or three cc. tannin solution (analytical strength) + 5-10 drops bromine water containing 4-5 grams bromine per liter.

As is generally known, catechol tans give a precipitate while pyrogallol tans do not. The delicacy of the test is very different with different catechol tans, and we have also found that presence of wood pulp prevents (or if present in smaller quantities diminishes) the precipitation. This is the case even if a considerable excess of bromine is used, and can therefore not be due to the presence of sulphites. We have also observed that the precipitate formed by catechol tans with bromine is redissolved by adding wood pulp solution.

H. SOLUBILITY TESTS.

It was suggested by Prof. Procter to determine the solubility of the different tannins in organic solvents by either shaking out the aqueous tannin solutions with a solvent, not miscible with water, or to precipitate the aqueous tannin solution by adding a solvent miscible with water. Both ways have been tried and proved very promising.

It must be mentioned that Hinrichsen and Kedesdy in their investigation of inks have determined the solubility of some tanning agents in ethyl acetate. Their

results were so encouraging, that we decided to start this part of our work by

1. Shaking out the aqueous solutions with ethyl acetate and by determining the soluble part in per cents of the total soluble.

We proceeded the following way:

Twenty-five cc. tannin solution (analytical strength) were shaken out with 25 cc. ethyl acetate in a small shaking funnel, the two layers allowed to separate and the aqueous layer run into a second funnel, where the shaking out with another 25 cc. ethylacetate was continued. This process was repeated until the ethyl acetate layer appeared quite colorless (2-5 times). Twenty cc. of the remaining aqueous layer were then evaporated, the residue dried until constant weight, and the difference between this weight and the residue of 25 cc. original solution expressed in per cents. of the original solubles.

This gave the solubility in ethyl acetate.

The results are given in Table III (first column).

It is clearly to be seen that different tannins differ widely in their solubility in ethyl acetate. This will specially be of interest for the distinction of different catechol tans, *e. g.*, quebracho and mangrove. The influence of sulphiting quebracho extract is also very distinct, and it can be seen that the more SO₂, the less solubles in ethyl acetate. By acidifying the tannin solution with acetic acid before shaking out with ethylacetate, somewhat higher figures are obtained; but they never come up to the figures of original quebracho (see figures in brackets). The fact that wood pulp is not or very little soluble in ethyl acetate is also worth mentioning. Applications of this test will be given later, but it may be said here, that much experimental work in this direction is needed, to corroborate the figures given here, to learn the limits for each tannin and to determine the influence of different methods of extract manufacture on the figures of one material. Further on other solvents than ethyl acetate have to be tried.

It would be interesting to investigate what percentage of tannins and non-tannins are shaken out with ethyl acetate; we have done such an analysis in one case, *viz.*, in the case of a quebracho extract. By shaking out 100 cc. of a 1-per cent. solution of a liquid quebracho extract four times with 100 cc. ethyl acetate, evaporating the ethyl acetate (at low temperature) and dissolving the residue in 300 cc. H₂O, bringing the aqueous layer as well to a volume of 300 cc., the analysis of these two solutions gave the amount of tans and non-tans which are soluble in ethyl acetate. We found:

Soluble in ethyl acetate	{ 90.56 per cent of the tans.
	{ 43.9 per cent of the non-tans.
	{ 77.7 per cent of the solubles.

Thus the solubility of the quebracho tans is about as high as the solubility of gallotannic acid (see Table III). (But they are not identical as can be seen from the acetic acid lead acetate test, which gives clear

solution with quebracho, but copious precipitation with gallotannic acid.)

Another solubility test was carried out by adding alcohol to the aqueous tan solution as follows:

Ten cc. tannin solution (6-8 times analytical strength) were put in a 100 cc. flask and alcohol (95 per cent.) added to the mark; after shaking the flask and allowing it to stand for about one hour, the precipitate was filtered, and 50 cc. of the filtrate evaporated, dried to constant weight and the difference between this weight and half of the solubles in 10 cc. of the original tannin solution expressed in percentage of the original solubles. This gave the alcohol precipitation figure.

The second column in Table III contains the results.

All catechol tans seem to give very low figures. The high figures of wood pulp may also be mentioned.

TABLE III.

	Soluble in ethyl acetate, per cent.	Precipitated with alcohol, per cent.
Quebracho 1.....	77.9	2.2
Quebracho 2.....	72.7	2.2
Quebracho 3.....	80.0	0.8
Sulf. Quebracho 1 (3.18 per cent SO ₂)..	33.6	4.7
Sulf. Quebracho 2 (4.3 per cent SO ₂)....	31.1 [44.1]	2.1
Sulf. Quebracho 3 (6.47 per cent SO ₂)...	23.9 [31.1]	1.1
Mangrove 1.....	4.9	6.8
Mangrove 2.....	0.0	1.3
Ulmo	26.0	1.6
Mimosa 1.....	34.2	2.3
Mimosa 2.....	37.9	0.0
Gambier (indragiri).....	51.4	4.8
Oakwood	2.0	26.7
Chestnut 1.....	3.0	21.3
Chestnut 2.....	10.1	17.4
Chestnut 3 (decolor).....	9.4	19.1
Myrobalans 1.....	33.3	9.3
Myrobalans 2.....	35.7	8.2
Myrobalans 3.....	44.4	8.2
Myrobalans 4.....	45.6	5.5
Valonia 1.....	7.3	38.6
Valonia 2.....	0.3	26.0
Sumach 1 (extract).....	50.7	14.8
Sumach 2 (extract).....	56.2	10.5
Sumach 3 (extract).....	57.7	9.8
Sumach 4 (Sicilian sumach).....	42.0	15.9
Divi-divi	49.7	1.8
Algarobilla	54.4	1.4
Pistacia	3.4	28.9
Gallotannic acid.....	91.8	0.0
Wood pulp 1.....	0.0	37.1
Wood pulp 2.....	0.0	52.2
Wood pulp 3.....	3.9	43.3
Wood pulp 4.....	3.9	71.7

¹Per cent. of solubles.

The remarks made with regard to the ethyl acetate figures may also be applied here; and it is to be hoped that the application of other organic solvents (acetone, methyl alcohol, etc., and mixtures) will lead to some more valuable figures.

Applications of Solubility Tests.—Only a few of them may be given as examples.

A pure unsulphited quebracho extract must give an ethyl acetate figure of 70-80 per cent. and an alcohol figure of less than 3 per cent.

Presence of wood pulp diminishes the first and increases the last figure considerably. Mixtures which we made prove this and show that the ethyl acetate

figure very nearly agrees with the figures calculated from the figures of the components.

	Ethyl acetate figure found.	expected.	Alcohol figure.
In 250 c.c. { 14 g. quebracho + 7 g. wood pulp }	44.4	46.9	21.5
In 250 c.c. { 20 g. quebracho + 2 g. wood pulp }	66.6	65.5	5.5

Thus, if unsulphited quebracho extract contains no pyrogallol tans (see formaldehyde test), and gives low ethyl acetate and high alcohol figures the presence of wood pulp is to be inferred.

If, on the other hand, the ethyl acetate figure is lowered, but the alcohol figure unchanged, and neither pyrogallol tans nor wood pulp found by the respective tests, the adulteration of the quebracho extract will be due to either mangrove or some other catechol tan (*f. i. ulmo*).

The following experiment, made on a mixture of quebracho and mangrove bears this out:

	Ethyl acetate figure found.	expected.	Alcohol figure.
In 250 c.c. { 11 g. quebracho + 7 g. mangrove }	38.9	37.4	3.3

The ethyl acetate figure is not only qualitative but also gives us an idea of the amount of adulteration in a quebracho extract.

Another application of the solubility tests applies to the detection of myrobalans in mixture with oakwood or chestnut extracts. The ethyl acetate figure will appear increased and the alcohol figure diminished.

A chemical detection of adulterations of sumach may also be carried out by this test, as is illustrated in the following table:

	Ethyl acetate figure found.	expected.	Alcohol figure.
Sumach	42.0	...	15.9
90% sumach + 10% pistacia.....	36.8	38.1	16.0
75% sumach + 25% pistacia.....	31.8	32.35	18.4
50% sumach + 50% pistacia.....	24.2	22.7	20.0
Pistacia	3.4	...	28.9

This may be useful as a supplement to the microscopical analysis, allowing us to assume the approximate amount of pistacia present. Sumach containing stems (and thus showing a smaller amount of tans by analysis) behaves like ordinary sumach (*e. g.*, 45.2

TABLE IV.

	Solubles.	Tans.	Non-tans.	Hydrolyzed solubles.
Quebracho	4.45	3.82	8.38	4.51
Quebracho	4.28	3.89	7.67	4.07
Mangrove	3.21	3.41	2.64	3.02
Ulmo	3.9	3.71	5.9	4.85
Ulmo	2.15	3.85	1.3	...
Mimosa	4.23	4.56	3.4	3.24
Gambier	2.93	3.07	2.73	2.78
Oakwood	3.32	3.9	2.14	2.4
Chestnut	3.95	3.5	5.8	2.8
Chestnut	4.36	4.55	4.35	...
Myrobalans	3.7	4.44	2.41	2.14
Sumach	4.1	5.58	1.58	...
Sumach	4.44	5.37	2.77	...
Sumach	4.66	6.3	1.6	...
Wood pulp.....	0.88	...	...	0.89
Wood pulp.....	0.96	...	...	0.89

per cent. ethyl acetate figure; 10.7 per cent. alcohol figure).

Several other applications of the solubility tests can easily be suggested after studying the table.

Attempts to Get Iodine Values of the Different Tannins.—The action of idoine on tannins has been studied by Boettinger,⁸ Jean,⁹ Boudet¹⁰ and lately by Hinrichsen and Kedesdy.¹¹ The last named authors investigated carefully the influence of different conditions on the iodine number of gallotannic and gallic acid, and they have worked out a method which gives reliable and concordant results, showing that one molecule of gallotannic acid combines with 16 atoms of iodine, while one molecule of gallic acid combines with 8 atoms of iodine.

We have adopted the method of Hinrichsen and Kedesdy, working in the following way:

Twenty-five cc. tannin solution (containing about 0.1 tannin) + 20 cc. iodine solution (about one-third normal) + about 2 grams NaHCO_3 were allowed to stand over night and then titrated back with one-third N-thiosulphate.

The same test was carried out with 30 cc. of the non-tan solution, which corresponds to 25 cc. of the above tannin solution. The figures thus obtained and the weights of the residues of solubles and non-tans allowed us to calculate how many grams iodine are taken up by (a) 1 gram solubles, (b) 1 gram non-tans (c) 1 gram tannin.

It was hoped that these figures would come out in good concordance when different samples of one tannin material or extract were used, and that different tanning materials would differ widely in their iodine numbers. This being the case, the iodine number would be a very valuable factor in the examination of tannins. Unfortunately our expectations were not realized by the experiment as can be seen from Table IV. We communicate these results in order to save the time of anybody who intends to work in this direction. Some few observations may also be mentioned which we made in the course of these experiments. We found that in the case of quebracho, mangrove, ulmo, gambier and pistacia lentiscus, a precipitate was formed with iodine and sodium bicarbonate, while the solutions of oakwood, chestnut, mimosa, myrobalans, sumach and wood pulp remained clear. The non-tans remained clear in all cases. This shows about the same classification as the Eitner-Philip test. The iodized solutions of all tannins no longer give tannin reactions; even the formaldehyde precipitation is not given by the iodized catechol tans. This proves that the iodine reacts with the hydroxyl groups, which is in concordance with Boettinger's statement that acetylated tannins do not take up any iodine.

We have also determined the iodine numbers of tannins, after boiling the solutions with alkali and

acidifying the hydrolyzed solutions with acetic acid. Fifty cc. of the tannin solution (analytical strength) were taken and 5 cc. sodium hydrate (40 per cent.) added, and the mixture boiled with the reflux condenser for two hours; then the solution was made up to 100 cc., 50 cc. out of it was taken, slightly acidified with acetic acid and treated with 25 cc. iodine solution and 2 grams sodium bicarbonate as before. We expected to see some valuable relation between this iodine number and the iodine number of the original solutions, assuming that the different splitting up products of the various tannins should behave differently against iodine. The last column of Table IV shows that even this expectation was not realized by this experiment.

We have therefore not continued the study of iodine numbers, though it is possible that the action of iodine on tannins may still be useful in some other way for the differentiation of tannins. If we, for example, take quebracho, dividing the solubles into those soluble in ethyl acetate and those which are insoluble, and then determining the iodine numbers in both parts, we might get some useful information not only as regards the difference in the behavior of these two parts to iodine, but also as to the analogy of the ethyl acetate fractions of different materials. In choosing a number of organic solvents, and determining the iodine values of the tans and non-tans of different materials soluble in these solvents, we might find corresponding figures which allow the conclusion that one component in the complex mixture of a tanning material is identical with one component in another tanning material. This of course means working in a somewhat different direction than was the original object of this paper.

Turning back to the promising tests mentioned above, we think it convenient to reproduce the behavior of the different tannins in table form (Table V). We trust that this table will not only help us considerably to distinguish a pure extract, but will also enable us in many cases to decide as to the nature of a mixture.

Before concluding, we wish to repeat once more that the results given above are only to be taken as a small step in the work of qualitative examination of tannins. Though the figures which we communicate are obtained by careful work and are reliable for the tannin extracts which we had in hand, we fully recognize the necessity that a far greater number of experimental figures of different samples must be obtained—by collaboration of many workers—in order to get reliable mean values, and limit values for each tannin and in order to learn the effect of different treatments of extracts even if no adulteration is added. We hope that this paper will give stimulation for such work.

The total production of coke in the United States in 1910 was 41,708,810 short tons, the production in 1911 was about 35,000,000 short tons.

⁸Chem. Zeitung, 1896, p. 984; 1897, p. 57 and 460.

⁹Ann. chim. anal. appl., 5, p. 134.

¹⁰Bull. Soc. Chim., 3, 35, 769, 1906.

¹¹Mitteilungen aus dem königlichen materialprüfungsamt. Gross-Lichterfelde, Berlin, 1907. See also Grassler, Coll., 1910, p. 408, and 1911, p. 46.

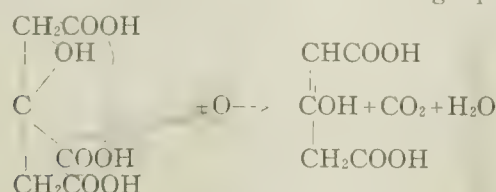
DETERMINATION OF CITRIC ACID.

The following matter on the determination of Citric Acid is reprinted from a recently issued circular of the Bureau of Chemistry, U. S. Department of Agriculture. This circular was prepared by David S. Pratt, Assistant Chemist, Division of Foods of the Bureau of Chemistry.

HISTORICAL NOTE.

At the present time there is no practical method for the determination of citric acid in the presence of other fruit acids. In the absence of other organic acids, barium citrate may be precipitated in a 50 per cent alcoholic solution. This precipitate may be filtered, dried, and weighed directly¹ or may be converted into barium sulphate and weighed as such.² When citric acid is accompanied by malic, tartaric, or some other similar acid, however, the procedure is very complicated and unsatisfactory. These other acids are at least partially precipitated with the citric, although, as Jørgensen³ points out, it is possible to effect a partial separation by precipitating the barium salts in 26 per cent alcohol. In this solution barium citrate is nearly insoluble and barium malate and tartrate rather soluble. Unfortunately the separation is very far from sharp, and the necessity of repeated reprecipitation makes the determination tedious and unsatisfactory. Methods based upon the evolution of carbon monoxid from citric acid when heated with concentrated sulphuric acid at 100° C.⁴ and upon precipitation of the citric acid by means of quinin⁵ are subject to the same limitations.

It has long been known that oxidizing agents in mineral acid solution break down citric acid with the production of acetone and carbon dioxid. Péan de Saint Gilles⁶ notes that potassium permanganate and sulphuric acid effect this change at temperatures above 80° C. Fleischer⁷ obtained no acetone, however, in the absence of mineral acid, and Phipson⁸ states that a solution of free citric acid at ordinary temperatures gives, with potassium permanganate, oxalic acid but no acetone. The work of these early writers was carefully gone over by Wöhlk,⁹ who found that the formation of oxalic acid is due only to secondary oxidation or to an excess of potassium permanganate, and that the first action of potassium permanganate on citric acid in acid solution is the formation of acetone dicarboxylic acid in accordance with the following equation:



The enol form is given, as the dicarboxylic acid reacts with acid ferric chlorid to give a reddish color¹⁰ characteristic of hydroxyl, but the keto form also exists, as the substance gives a red color in alkaline solution with sodium nitroprussid.^{11 12} These reactions are offered by the authors quoted as qualitative tests for citric acid, but they require much time and careful manipulation.

Stahre's¹³ test is comparatively simple. It consists in acidifying the solution to be tested with sulphuric acid, adding bromin water, and heating with potassium permanganate. A white turbidity results in the presence of citric acid. Wöhlk⁹ has shown that here again the test depends upon the formation of acetone dicarboxylic acid, and that this in the presence of bromin precipitates panta-bromacetone as a white milky cloud.

The most delicate and satisfactory test for citric acid is that proposed by Denigès.¹⁴ His reagent is made by dissolving 5 grams of mercuric oxid in 20 cc of concentrated sulphuric acid and diluting with water to 100 cc. When this reagent is added to a solution containing citric acid or a citrate, the solution warmed and a potassium permanganate solution slowly added, a white precipitate is formed, characteristic of citric acid. This is due to the formation of a complex between the reagent and the acetone dicarboxylic acid resulting from the oxidation of citric acid. Malic, tartaric, and other ordinary fruit acids give no precipitate; oxalic gives a precipitate upon addition of the reagent, but by filtering and adding potassium permanganate to the clear filtrate the interference is avoided. This test is explained in detail by Yoder¹⁵ and need not be elaborated upon here. It should be noted, however, that it often fails in the presence of much sugar. In this event the citric acid must be separated and freed from the interfering substances by precipitation as barium citrate in 50 per cent alcoholic solution, washed with 50 per cent alcohol, and liberated by sulphuric acid. To the clear filtrate so obtained the test is applied. The test solution should be diluted until a few drops of potassium permanganate solution will give a faint color in the cold. The pink liquid is then heated. In the presence of citric acid the color fades and is replaced by a white turbidity characteristic of citric acid. If this is not obtained add potassium permanganate drop by drop, waiting between each addition until a clear solution free from manganese dioxid is obtained.

It has been suggested by Beau¹⁶ that this method might be made quantitative for citric acid in milk. His idea was to mix the milk with Denigès's reagent, heat nearly to boiling and add drop by drop a 1 per cent potassium permanganate solution. A slight excess, later destroyed by hydrogen peroxid, was used, the precipitate dried and weighed. Theoretically this meth-

¹Bacon and Dunbar. U. S. Dept. Agr., Bureau of Chemistry Cir. 78, p. 8.

²Crcuse. Jahresber. Chem., 1873, p. 970.

³Zts. Nahr. Genussm., 1907, 13:241; 1909, 17: 396.

⁴Spica. Chem. Ztg., 1910, 34:1141.

⁵Sindet. Bull. Soc. chim. Par., 1896 (3), 15:1162.

⁶Jahresber. Chem., 1858, p. 583.

⁷Ber. d. chem. Ges., 1872, 5:353.

⁸J. Chem. Soc., 1862, 15:141.

⁹Zts. anal. Chem., 1902, 41:77.

¹⁰Favref. Ann. chim. anal, 1908, 13:177.

¹¹Bernh. Merk. Pharm. Ztg., 1903, 48:894.

¹²Spica. Gaz. chim. ital., 1901, 31(2):61.

¹³Nordisk. Farm. Tidsskrift, 1895, p. 141; Zts. anal. chem., 1897, 36:195.

¹⁴Ann. chim. phys., 1899, 18:415.

¹⁵J. Ind. Eng. Chem., 1911, 3:644.

od is faulty, it being impossible completely to oxidize citric acid to acetone dicarbonic acid without at the same time carrying the reaction further. In fact, Wöhlk¹⁷ found that acetone dicarbonic acid alone breaks down in aqueous solution at 0° C., giving acetone and carbon dioxide. It is evident, therefore, that no method based upon the partial oxidation of citric acid can be quantitative.

This suggested, however, the final attack on the problem. If citric acid could be quantitatively oxidized to acetone, this might be easily removed from the other products of the reaction by distillation and determined. From the results of Péan, Fleischer, and Wöhlk it appeared that the oxidation should be carried on in acid solution in order to give acetone as the final product. It is evident that all acetone dicarbonic acid formed will break down at the temperature of distillation, giving acetone.

EXPERIMENTAL WORK.

A number of oxidizing agents were tried on known amounts of citric acid in solutions acidified with various mineral acids. Of all the combinations experimented with, a solution of potassium permanganate acting in the presence of sirupy phosphoric acid was most satisfactory. Sulphuric acid under some conditions is partially reduced to sulphuric dioxide, and this gives a precipitate with Denigès's reagent. Hydrochloric acid must be avoided, as it dissolves the final precipitate. Potassium bichromate decomposes citric acid in acid solution, yielding acetone, but is less satisfactory than permanganate. The great advantage possessed by phosphoric acid over sulphuric acid will be touched upon later. With certain precautions described under details for carrying out the method, a solution containing 0.5 gram of potassium permanganate per liter gave very good results.

At this point it became necessary to decide upon the best method for determining acetone in the distillate. The ordinary methods depending on iodine solution are not well suited to this case, inasmuch as other volatile bodies are generally present that are also oxidized by an alkaline iodine solution. A very satisfactory gravimetric method was introduced by Denigès.¹⁸ His mercuric sulphate reagent described above forms with acetone an insoluble white precipitate similar in appearance to that formed with acetone dicarbonic acid. The method as given is to heat a very dilute acetone solution, containing not over 1 gram of acetone per liter, with the reagent in excess in a sealed flask immersed in boiling water. The precipitate is dried at 100° C., and its weight multiplied by the factor 0.06 to obtain the corresponding amount of acetone. To the precipitate so obtained, Denigès gives the formula $(2\text{HgSO}_4 \cdot 3\text{HgO})_3 \cdot 4\text{CH}_3\text{COCH}_3$, with a theoretical factor of 0.0584. He further states that long-continued

heating at 110° C. causes the loss of acetone, giving the compound $2\text{HgSO}_4 \cdot 3\text{HgO} \cdot \text{CH}_3\text{COCH}_3$.

However, as Oppenheimer¹⁹ points out, no analyses of the product dried at 100° C. and utilized in the determination are given. In fact, Oppenheimer arrives at a different composition and an acetone factor of 0.052. He states that the compound does not lose acetone at 110° C., but hesitates to state definitely its formula. From these results it is evident that an empirical factor must be used to convert the weight of precipitate into terms of citric acid. Table I gives the determinations used in arriving at this factor and the calculated amount of citric acid when using it. The method employed in obtaining these results is explained in detail later.

TABLE I.—DETERMINATION OF FACTOR.

Amount of citric acid used.	Weight of precipitate.	Calculated factor.	Citric acid found by using factor 0.220.
Gram.	Gram.		Gram.
0.020	0.104	0.187	0.023
.049	.234	.208	.051
.052	.227	.224	.050
.080	.343	.231	.075
.097	.453	.214	.100
.104	.430	.240	.094
.104	.451	.229	.099
.104	.445	.232	.098
.104	.442	.234	.097
.107	.510	.210	.112
.128	.559	.229	.112
.128	.556	.230	.122
.146	.679	.215	.149
.246	1.181	.208	.259
.491	2.364	.208	.520
.046	.213	.216	.049
.049	.220	.221	.048
.050	.231	.216	.051
.049	.205	.239	.045
.050	.211	.237	.040
.096	.468	.205	.103
.096	.437	.219	.096
.049	.208	.235	.046
.049	.225	.218	.050
Average		.220	

THE METHOD.

The apparatus needed is very simple and consists of a 500 cc distilling flask connected with a condenser, preferably of the spiral type. A small dropping funnel is inserted in the neck of the flask, protruding about half an inch through the stopper and drawn down to the dimensions of an ordinary medicine dropper. A longer tube is apt to form bubbles of steam which force the remainder of the potassium permanganate rapidly into the flask and thus interfere with its regular addition, which should be drop by drop. This allows the acetone formed in the reaction to be distilled off as fast as formed, thus preventing any loss by oxidation. To make this doubly sure, some device should be included in the flask to cause steady ebullition. For this purpose nothing is better than a glass rod with half an inch of small tubing sealed on the lower end. It is essential that the small hollow end be filled with air

¹⁷Rev. gén. du lait, 1904, p. 386.

¹⁸Loc. cit.

¹⁹Ann. chim. phys., 1899, 18:400; Compt. rend., 1898, 127:963, 1898: 126:1868.

¹⁹Ber. d. chem. Ges., 1899, 32:986.

when the heating of the liquid is commenced. After cooling this cavity fills with liquid, which should be shaken out before using. The device is not new, but it does not receive the recognition it merits in many cases where regular boiling without bumping is desired. The distillate is received in a liter Erlenmeyer flask containing 30 to 40 cc of Denigès reagent.²⁰ This is made as follows: Add about 500 cc of water to 50 grams of mercuric oxid; then add 200 cc of concentrated sulphuric acid with constant stirring, and heat the mixture, if necessary, on a steam bath until the solution is complete. After cooling, make up to a liter and filter.

The method of analysis is as follows: If a fruit juice is under examination, weigh 50 grams into a beaker and add 110 cc of 95 per cent alcohol to throw out the pectin bodies. After standing 15 minutes remove these by filtration* and wash the residue with 95 per cent alcohol in which citric acid is readily soluble. Dilute the filtrate with water to give approximately a 50 per cent alcohol content and add enough 20 per cent aqueous solution of barium acetate to precipitate the barium citrate completely. Stir, let stand until the precipitate partially settles, and filter. Wash the precipitate thoroughly with 50 per cent alcohol to remove the greater part of the sugar present. This may be done by filling the paper twice with the dilute alcohol. Place the filter paper and its contents in the beaker used for the precipitation and dry until all alcohol is removed. If desired, the same result may be accomplished by washing with ether before removing the filter paper from the funnel. Add about 50 cc of water and from 3 to 5 cc of sirupy phosphoric acid to the beaker containing the filter paper and precipitate. Upon warming, the barium citrate is completely dissolved. This is the chief reason for the use of phosphoric acid rather than sulphuric, which would throw out barium sulphate. Filter into a 100 cc measuring flask and make up to volume with washings from the filter paper in the beaker. This completely removes the barium citrate.

An aliquot, estimated to contain from 0.050 to 0.150 gram of citric acid, is measured into the distilling flask. About 5 to 10 cc of sirupy phosphoric acid and 400 cc of hot water are added. When briskly boiling, add potassium permanganate solution (0.5 gram per liter), 1 to 2 drops per second, until a pink color throughout the solution shows the reaction to be complete. The distillate is received in a liter Erlenmeyer flask containing from 30 to 40 cc of Denigès's reagent just described. The distillation is continued until about 50 to 100 cc remain in the flask. The Erlenmeyer containing the distillate is then connected with a reflux condenser, and boiled gently for three-quarters of an hour after the solution turns milky. Filter

hot through a Gooch crucible, wash with water, alcohol, and finally with ether, and dry in a water oven for half an hour. The weight of the precipitate multiplied by 0.22 gives citric acid.

With many solutions the precipitation of the barium citrate and its subsequent solution are unnecessary. In cases, however, where large amounts of sugar are present it is the safer procedure, and as the whole operation requires but little time and attention it is to be recommended. The presence of sugars seems to retard the oxidation of the citric acid, and moreover makes it difficult to determine when enough potassium permanganate has been added, as no definite end point can be reached.

The precipitate obtained in this method is heavy and never causes any difficulty in filtering. It is a creamy white if properly obtained, and is very insoluble in hot or cold water, in alcohol, and in ether.

TABLE II.—DETERMINATION OF CITRIC ACID IN THE PRESENCE OF TARTARIC AND MALIC ACIDS.

Citric acid used. Gram.	Malic acid present. Gram.	Tartaric acid present. Gram.	Weight of precipitate. Gram.	Citric acid recovered Gram.
0.050	0.000	0.010	0.230	0.051
.050	.000	.019	.235	.052
.050	.000	.096	.242	.053
.050	.046	.000	.230	.050
.050	.093	.000	.228	.050
.049	.057	.000	.245	.053
.052	.010	.000	.246	.054
.052	.047	.000	.230	.051
.053	.094	.000	.240	.053
.050	.048	.050	.215	.047
.050	.048	.050	.224	.049

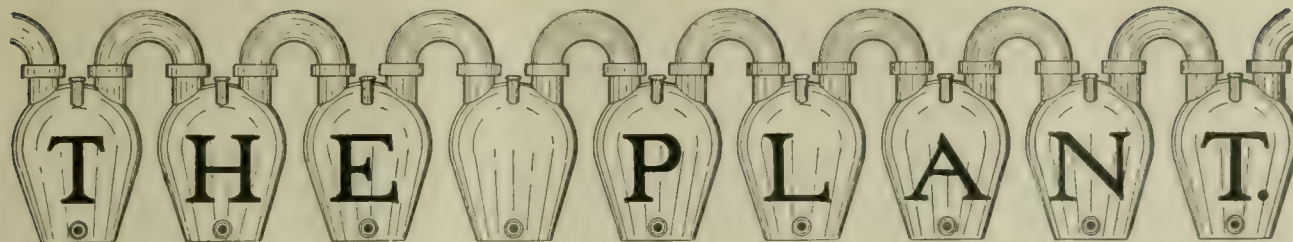
The crucibles and flasks may be readily cleansed by using dilute hydrochloric acid in which the precipitate is easily soluble. Malic and tartaric acid do not interfere with the determination as may be seen in Table II.

The method is suited to the analysis of a great variety of substances besides fruits and fruit products. Among these might be mentioned citric acid in the presence of sulphuric acid or in crude calcium citrate, both occurring in the commercial manufacture of this acid; also various medicinal preparations, flavoring extracts, and any material containing citric acid. Duplicate results generally check to within 2 or 3 mg. of citric acid.

The results of the Canadian Government's experiments in the production of fuel from the peat bogs of Alfred Township, Prescott County, have been so successful that the Canadian Pacific Railway has opened negotiations with the Government for the purchase of these bogs. Should the railway company secure the property, it is understood that the output of prepared peat will be greatly increased, and that Montreal will be one of the cities selected in which to sell the fuel.

²⁰Loc. cit.

*A folded filter is satisfactory when but little citric acid is present, as in the case of fruits, and saves much time. The pectin bodies generally may be retained in the beaker and washed by decantation.



MANUFACTURE OF C. P. NITRIC ACID.*

Nitric Acid is made from sodium nitrate and sulfuric acid according to the following formula: $2\text{NaNO}_3 + \text{H}_2\text{SO}_4 = 2\text{HNO}_3$.

The proportions given in the formula, however, are not followed in actual practice, for instead of using 170 parts NaNO_3 and 98 parts H_2SO_4 , about equal weights of each are taken, and the residue instead of being a normal salt (Na_2) is a mixture of the normal and the acid salt. (NaHSO_4 .) There are two reasons for using these proportions; in the first place if less sulfuric acid is used, a higher temperature is necessary to complete the final decomposition of the nitrate, and as a result a large amount of N_2O_2 is formed instead of HNO_3 , secondly, the excess of H_2SO_4 prevents the solidifying of the residue and permits it being drawn from the retort in a fluid state.

The apparatus for making nitric acid is simple in construction and the manufacture can be conducted



Fig. 1.

economically on a comparatively small scale. The principal reason for this is that there are no volatile gases to contend with and the condensation of the acid vapors is rapid and complete. The residue, also while it is practically a waste product, in a small plant, because it does not pay to work it up into a neutral salt on a small scale, can be disposed of at a low price for the free H_2SO_4 which it contains.

The retort in which the operation is conducted is made of cast iron, and as strong sulfuric and nitric acid vapors have very little action on cast iron when it is hot, the retort will last many years with careful management. The retort is enclosed within the furnace and completely surrounded by hot gases from the fire, so that the entire surface is heated.

Fig. 1 represents a longitudinal section of the furnace and the retort (R) is a cast iron cylinder 6 ft. long by 5 ft. diameter with flanged ends to which are bolted cast iron heads, the joints being either surfaced true or luted with acid proof cement.

The retort is supported upon legs projecting into the brickwork and is placed so that it is surrounded

by hot gases from the fire (F). An opening 12 ins. in diameter on top (C) flanged and closed with an iron plate with a clay joint, is used for charging the nitrate and the sulfuric acid. A 4 in. pipe at (B) projecting through the wall and closed with removable plug is provided for discharging the residue after the operation is completed. The vapors of nitric acid are conducted off through an opening at the top of the retort to which is connected an earthenware pipe (E).

The condensing system is constructed as shown in Fig. 2; A^1 and A^{11} are earthenware or porcelain pipes, each made with a row of openings on one side into which are inserted a series of glass tubes (C) about $1\frac{1}{4}$ ins. in diameter by 6 ft. long, the joints being packed with pure asbestos. Condensation is effected

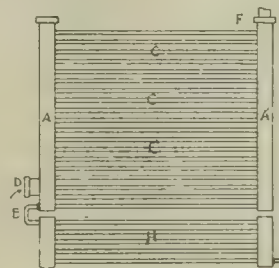


Fig. 2.

in these tubes either by trickling water over the surface from a perforated pipe overhead which delivers the water onto the top tube from which it trickles down over the tubes beneath, or, if a large number of tubes are used so as to increase the condensing surface, the condensation can be easily accomplished by the cooling effect of the air.

This condensing system was originally patented and is known as the Hart condensing system, but the patent, the essential feature of which was the use of water for cooling purposes, has now expired. The objections to the use of water is the liability of breakage due to the effect of cold water on the hot glass: this difficulty is overcome by the method of air cooling, but the advantage gained is partly offset by the possible loss of acid due to leakage from the greater number of joints.

The nitric acid vapor from the retort is lead into the pipe (A^1) at D and is divided in its path through the condenser by the glass tubes (C, C, C,) where the heat is absorbed either by the water trickling down over the tubes or by radiation into the air. The condensing tubes are slightly inclined towards the end nearest the retort, consequently the acid as it condenses flows back and falls to the bottom of the pipe (A^1) and runs off

*From The Chemist Analyst.

to a receiver through the connection at (E). This reflux arrangement of the system bringing the liquid as it leaves the condenser into direct contact with the hot vapors from the retort, prevents the absorption of chlorine which is formed from the sodium chloride always present in small amounts in commercial nitrate, as well as hyponitric acid formed by a slight decomposition of the nitric acid in contact with the hot iron retort. The chlorine and hyponitric acid pass out through the opening at the top of the pipe (A^{11}), whence it may be lead off through a lower, where the hyponitric is converted into nitric acid by oxidation in a current of air.

To avoid danger of cracking the receiver, which for convenience in handling the acid by air pressure, is a strong earthenware blow case set in the ground, the hot acid is cooled by running through a series of glass tubes (H) sprinkled with water, the tubes being constructed with a lip at one end and closed at the other

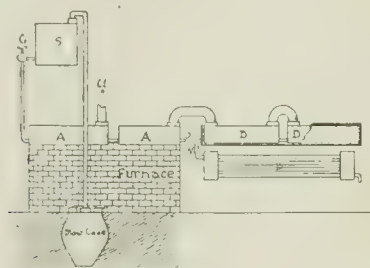


Fig. 3.

end, with an opening on the upper side of the tube directly underneath the lip of the tube above.

The charge placed in the retort consist of 1,800 lbs. of nitrate of soda and 1,750 lbs. sulfuric acid and the decomposition of the mixture commences as soon as heat is applied, the first distillate having a temperature of about 80°C , which gradually rises to 128° at the end of the run. The strength of the distillate is about 100 per cent HNO_3 at the start but gradually decreases as the operation advances and the very last distillate is not over 25 per cent, the average strength of the entire run being about 86 per cent. This distillation proceeds very rapidly during the first part of the operation but gradually decreases towards the end until finally the acid only drips; then the fire is drawn from under the retort and the residue run off into an iron pan to cool and solidify.

The acid thus made contains iron, sulfate, chlorine, iodine and hyponitric, and to be purified must be re-distilled in glass or porcelain vessels. The apparatus used for this purpose represented in Fig. 3 is made of porcelain. The acid is elevated by air pressure to the vessel (S) and then runs by gravity to the stills (AA^1) the flow being regulated by a cock at (G). The vessels forming the stills, of which there are several, are connected together so that the acid flows through them successively and at the farther end there is a slight overflow (O) to carry off the impurities which become concentrated in the tailings as the acid distills off. As the chlorine and the hyponitric acid distill off at a com-

paratively low temperature, arrangements are made to separate these vapors, which, if the supply of acid is properly regulated are entirely distilled off in the first vessel and prevented from contaminating the pure distillate, by being condensed in a separate condensor.

The pure acid is condensed in vessels (BB) immersed in a bath of running water and is drawn off at (N) hot and bleached while running through the cooler (D) and at the same time reduced to the proper strength for ordinary use (Sp. Gr. 1.42) by adding distilled water in a properly regulated stream.

The acid thus obtained is chemically pure and ready for shipment as soon as bottled.

The River Amazon, according to a report entitled "The Data of Geochemistry," published by the United States Geological Survey, carries annually to the ocean 618,000,000 metric tons of solution and sediment, and its turbidity can be observed in the ocean waters over 100 miles from the land.

The U. S. Consul at Reichenberg, Austria, reports an invention for a process of treatment of common straw whereby it is now possible to secure therefrom a fiber suitable for spinning. While the entire method is not revealed, it appears that the straw is reduced to a jelly-like substance by boiling, causing the separation of the fiber from the outer shell, and the fiber is then treated in hot-air machines. To this product is added another fibrous material, but never more than 20 per cent, so that fully 80 per cent is straw. The resulting "stuff" has many of the characteristics of the "fore" yarn used in jute spinning. The principal advantages claimed by the inventors are that the new fiber has all the merits of the yarns now produced; that the cost is only one-half that of similar products; that the weight is 40 per cent less; and that the goods are in every way desirable.

During January 214,749 acres of land in the state of Idaho believed to be underlain by phosphate rock were withdrawn on recommendation of the United States Geological Survey. This makes a total outstanding withdrawal in Idaho of 1,167,137 acres of phosphate land. In Wyoming 1,266,668 acres are now withdrawn as phosphate land, in Utah 107,745 acres, in Montana 33,950 acres, and in Florida 35,640 acres, a total of 2,611,140 acres. Partial detailed surveys of these areas made by Survey geologists show a very large quantity of this important fertilizer, the value ranging up into the billions of dollars. The Director of Survey, in his latest annual report, calls attention to the need of the enactment of a law that will permit development of this resource, which is coming more and more into use as an agricultural soil stimulant. The United States is believed to have the greatest phosphate deposits in the world.

COLORS AND THEIR APPLICATION TO LEATHER.*

By H. C. MERRILL.

In talking to you today about dyestuffs and their application to leather, I am going to briefly outline the different general classes of dyestuffs and the methods used in their application. Then I will consider hurriedly some of the more important kinds of leather in which the appearance of the color makes a large part of the value of the leather, for the purpose of pointing out the most successful methods of producing the best results.

Coal tar dyestuffs will be considered today under the divisions of:

Basic Dyestuffs.

Acid Dyestuffs.

Diamine or Cotton Dyestuffs.

Anthracene, Alizarine or Mordant Dyestuffs.

Dyestuffs, Diazotized and Developed on the Fibre.

Immedial or Sodium Sulphide Dyestuffs.

Dyestuffs Oxidized on the Fibre.

I have omitted entirely the dyestuffs commonly known as *Vat Colors*, as, for example, indigo or hydron blue, because they are not suitable for application to leather.

I shall also mention the dyewoods only in their capacity as mordants for basic dyestuffs and as tanning agents because their usefulness as coloring agents has been superseded by the coal tar dyestuffs, with the exception of logwood for black leather. Even logwood is fast losing its usefulness because of the acid, diamine and developed blacks which give stronger and better feeling leather.

In this talk I shall mention only names of dyestuffs made by Leopold Cassella & Co., Frankfort, Germany, because, being in their employ, I am more familiar with them and know their peculiar properties better than the dyestuffs of other manufacturers. Also the time allotted to me for this talk limits me, so that I shall only be able to mention the most important members of the various classes of dyestuffs.

Basic Dyestuffs are the most commonly used because leather was formerly made almost entirely with vegetable tanning materials. They are also entirely suitable for chrome leather after it has been properly mordanted with a vegetable tanning material.

Basic colors are best dissolved by mixing them thoroughly with cold water, and then raising to a boil with a steam jet. Cold water is best used because basic dyes often contain material which is liable to cake if the dyes are put into hot water. Auramine should not be dissolved in water over 175° F.

If the water is hard, the dyes should be wet with acetic acid before the water is added. Diamond phosphines which are not affected by the hardness of the

water, may be dissolved without the addition of acetic acid.

Phosphines were formerly made by the purification of a byproduct of magenta. The new phosphines like diamond phosphines are made synthetically and are much purer compounds.

Basic dyestuffs as a class are not very fast to light. Many acid, anthracene and diamine colors are much superior to basic colors in this respect. It is, however, practically impossible for the dyer of leather to secure such excellent results as are possible for the textile dyer because the tanner cannot fix his colors by boiling heat.

Phosphine, thioflavine, diamond phosphine, Bismark brown, safranine, methylene blue and new blue are the fastest to light of the basic colors.

Auramine, chrysoidine, fuchsine, methyl violet and solid green crystals are the deepest penetrating of the basic dyes.

Basic colors are much improved in their fastness to fat liquoring and finishing if after-treated with tartar emetic, potassium titanium oxalate or bichromate of potash. These salts also make the basic dyes color the leather more level if the bottom is fixed with them before dyeing.

Acid Colors are used on both vegetable and chrome tanned leather. They readily dissolve without any addition of acid. They do not require any mordant, but the depth of color is much increased by the addition of sulphuric or formic acid to the dye bath. The most level dyeings are obtained by adding the acid towards the end of the dyeing operation. However, the use of any acid is undesirable, especially on chrome leather, if after dyeing the leather has to be fat liquored with an alkaline emulsion of oils because the acid is liable to cause greasy spots by curdling the fat liquor.

Some of the most easy levelling acid colors include acid yellow A T, orange extra, azo orseille B B, lanafuchsine S B, cyanole F F, cyanole fast green G. These colors are quite fast to light, and also very easily soluble which causes them to easily penetrate the leather and produce very level shades. They are excellent for making light pearl and ecru shades, but are not suitable for dark shades.

Fast acid yellow 3 G, milling yellow O, brilliant crocein A Z, brilliant lanafuchsine G G and B B, alizarine cyanole E F and naphthol green B are extremely fast to light. Even anthracene colors are not any better for fastness to light than these colors.

Acid colors which are in most common use are Indian yellow G, orange extra, Havana brown S concentrated, scarlet E C, brilliant crocein M O O, fast red B, bordeaux, formyl violet S 4 B, water blue, brilliant milling blue B, pure soluble blue, solid blue, nigrosine, acid green, naphthalamine black, naphthol black and naphthol blue black.

The most important of these colors is nigrosine, which is used to produce blue blacks on vegetable and chrome tanned leather for making seasons for finish-

*Paper read at the Washington Convention of American Leather Chemists, Dec. 7, 1911.

ing black leather, and blackings for polishing shoes.

Acid colors are used extensively on vegetable and chrome tanned leather as a bottom for basic dyes, which they precipitate, to produce full, level colors. Their greatest success in fancy shades has been in making golden brown glazed kid, where they are used on chrome tanned goat skins, bottomed with fustic and logwood.

Acid dyestuffs are not firmly fixed on the leather by any process. They have a tendency to bleed off in the fat liquor, wherein lies one of the greatest objections to their use.

Diamine Colors have secured an important place for themselves in dyeing chrome leather. They attach themselves directly on chrome leather without any mordant, but they have only a slight affinity for vegetable leather for which reason they dye chrome leather better if it has not been retanned with any vegetable tanning agent.

Diamine colors are most readily soluble in water. Unlike basic colors they are less soluble in acid solutions and become more soluble when alkali is added to the dye bath. Because of this characteristic, chrome leather should be as nearly neutral as possible before dyeing, in order to secure level colors, and the dye bath does not need to be acidified even at the end of the dyeing operation as the colors exhaust completely, with the exception of colors dyed with very large percentage of dyestuffs.

Diamine fast yellow F F, diamine fast orange E G and E R, diamine fast brown G and R, diamine fast red 8 B L, diamine fast bordeaux 6 B S, diamine fast blue F F B, diamine fast brilliant blue R, are extremely fast to light and are equally as good as anthracene colors. Diamine catechine B, G and 3 G, diamine black B H, diaminogene extra, diamine fast red F, diamine fast yellow B are excellent dyes for chrome leather.

Diamine colors are often improved in respect to their fastness to vat liquor by an after-treatment with bichromate of potash or copper sulphate. They seem, however, to be affected detrimentally by iron salts.

Some diamine colors seem to work better in the dye bath if 2 per cent to 3 per cent of salt is used.

Oxy diamine blacks are the most important of the diamine colors in use. They have come into important competition with logwood and nigrosine on chrome leather only. They do not make a black as cheaply as logwood but do not make the leather as tender nor as harsh feeling as logwood. Oxy diamine black is slightly cheaper to use than nigrosine and does not bleed in vat liquor as the latter does. If these blacks are used with logwood, they give their greatest coloring power, if dyed on the leather before the logwood.

Diamine colors give excellent shades on chrome leathers which are finished without glazing on the grain or given an ooze finish on the flesh side. They are much faster to light than basic colors. When they are topped with basic dyes they produce a combina-

tion which is fast to light and has the fullness of the basic dyes.

Anthracene or Mordant Colors have been used to some extent on chrome leather because they are the fastest colors to light which have been produced. Many of this class of colors are unsuitable because the color is not developed except at a boiling temperature, as for instance alizarine red, which is a yellow until developed by chrome at boiling temperature. Different chemicals, such as bichromate of potash and potassium titanium oxalate, have been proposed to take the place of boiling heat, but they have been only partially successful. However, some of the mordant colors develop cold, while others give shades which, though undeveloped, are useful. These colors as a class are usually dull and are much improved if topped with basic colors.

The yellow anthracene colors such as anthracene yellow B N and C are the most important of this group.

Colors Which Are Developed on the leather have become prominent of late in the coloring of black ooze which requires much fullness of color. Other developed colors could be used for other shades in which fullness would be especially desirable, but the process is quite long and tedious and does not give colors that are any faster to light than basic dyes, which are applied much more simply. They are used at present only on chrome leather. The practice of diazotizing and developing seems to increase the softness of the leather, which is particularly beneficial in making ooze leather. The process is also carried out as cold as possible, with the exception of the dyeing at the beginning, so that the leather does not undergo the risk of being damaged. The entire process will be treated fully under the subject of black ooze on chrome tanned calfskins.

Immedial Colors are dyestuffs which are soluble only in sulphide of sodium. They have never found much use on chrome or vegetable tanned leather because they had a tendency to make the leather tender. They have been recommended for dyeing oil-tanned chamois leather. For this purpose equal parts of the immedial color and sodium sulphide crystals are dissolved in boiling water. After the solution is cooled, add 1/10 of formalin and 1/5 of soap. The chamois leather is drummed in this solution then re-vat liquored. These colors are very fast to washing.

Colors Produced by Oxidation on the Fibres are used for fur dyeing. For this method of coloring two chemicals ferrol B and ferrol S crystals come into extensive use. The wool or fur skins are first treated with a strong lime solution to remove the grease and dirt. Then the lime is removed and the wool or fur is treated cold with an oxidizing mordant composed of bichromate of potash, or sulphate of iron or copper and tartaric acid. The mordanting process varies with the kind of fur skin, and the shade to be obtained. Then the furs are rinsed thoroughly and dyed with ferrol B

or ferrol S crystals or a mixture of them and with the addition of hydrogen peroxide, ammonia and sometimes pyrogalllic acid. By varying this process, various full even shades of brown, grey and black can be very successfully obtained. The process is carried out cold so that the skins are not damaged. They also give good fastness to light.

Dyestuffs for Leather Finishes must be selected to mix properly with the other materials in the finish.

Glaze Finishes which are composed of solutions of albumen, casein, gelatin, gums, decoctions of seeds and moss, soap, oils and waxes, and alkali must be colored with acid dyes, the most important being nigrosine. Whenever the finish is alkaline, acid dyes must be used. This also applies to alkaline solutions of shellac and casein.

Shellac Solution in Alcohol must be colored with basic dyes, which are nearly all soluble in alcohol.

Collodion Varnishes are colored with cerasine colors, which are soluble in amyl acetate solutions.

Creams composed of soap creams and turpentine creams must be colored with cerasine colors, which have been treated with stearic acid.

In coloring the different kinds of leather for special purposes, if the best results are to be obtained, (1) the leather must be properly prepared to receive the dyestuff; (2) dyestuffs must be selected which are best suited to the kind of leather and for the shade to be dyed; (3) the processes, through which the leather must pass after dyeing, must be chosen and arranged to be least injurious to the color, and produce the desired result; (4) and great care must be taken in every process.

Chrome Tanned Calfskins are finished into several fancy leathers. The most important are the boarded tan calf, chrome Russias, and OOZE in black and fancy shades. The skins for boarded tan calf and chrome Russia are selected out of the tanned condition and colored while wet. The skins for ooze are vat-liquored after tanning with an emulsion of egg yolk and flour and then dried out, after which they are sorted and colored.

The fancy ooze colors can be made by bottoming with sumac or fustic extract and some mordant like sulphate of iron, tartar emetic, or potassium titanium oxalate, then coloring with basic dyes; or by coloring with acid or diamine dyes and sometimes topping with basic dyes. Some light shades are also made with pigments. Black ooze is made with a combination of logwood, nerazine or oxy diamine black and leather black, or with a combination of developed black and leather black.

Black Ooze Calfskins can be made with developed black as follows: This process also illustrates the use of developed colors. The chrome tanned calfskins are sorted after washing out of the chrome tannage. The skins are shaved and vat-liquored thirty minutes with 5 per cent egg yolks and 10 per cent flour. The skins are then drained off, hung up and dried. When dry,

the skins are dampened in sawdust, staked and buffed. Then they are ready for coloring. The skins must be buffed very clean so that after they are colored they will not need to be buffed a second time.

The skins for dyeing are thoroughly wet up thirty minutes in a drum of water at 140° F.

First, dyed 30 minutes at 130° F. with 12½ per cent diamine ooze black C R.

Then fixed 15 minutes with 5 per cent muriatic acid.

The skins are now drained off and rinsed in cold water.

Then diazotized, running first five minutes in 10 per cent muriatic acid.

Then add and run 15 minutes in 5 per cent nitrite of soda.

Then the skins are drained off and washed thoroughly.

The muriatic acid is given before the nitrite of soda because the latter has an alkaline reaction, which has a tendency to wash the black from the leather before it can be diazotized. The diazotizing must be done cold so that the nitrous gas will not escape easily from the solution.

The skins are now developed 15 minutes with 0.8% phenylene diamine dissolved with 1.6% soda ash, and 0.2% betanaphthol dissolved with 0.2% caustic soda.

The two solutions are made separately but are mixed before giving them to the skins.

The skins are then drained off and washed and then topped with 2% leather black No. 60763, ½% acetic acid.

The skins are then thoroughly rinsed off and vat-liquored forty-five minutes with 2% acid vat-liquor.

They are then dried on hooks, dampened in sawdust, staked, dry-milled, and tacked out.

Chrome Russias and Tan Boarded Chrome Calf are colored in about the same manner. Tan boarded is glazed so that it is necessary to keep these colors lighter and yellower because the glazing bakes them sadder and redder. These colors are usually made with basic dyes on top of a vegetable bottom, because they give very full, even shades. Acid and diamine colors can be selected which would be much faster to light.

Basic dyes are usually applied as follows:

Skins are first neutralized 20 minutes with ½ per cent borax and rinsed thoroughly.

Then bottom 30 minutes with 5 per cent fustic or sumac extract.

Fix the bottom 20 minutes with ¼ per cent tartar emetic or potassium titanium oxalate. Drain off and rinse.

Dye 30 minutes with a mixture of diamond phosphine G G, R, or D, Bismark brown E E, new blue R.

Set the dye 15 minutes with ⅓ per cent bichromate of potash.

Vat-liquor with 6 per cent acid vat-liquor.

Chrome Tanned Goatskins are mostly finished into black or colored glazed kid, or patent kid. Black glazed kid or patent kid are colored with logwood

and a mineral striker composed of an iron, copper or titanium salt, or a combination of them, and very often are topped with nigrosine or diamine black and methyl violet. The glazed kid manufacturer is very firm in his conviction that he must have a vegetable retannage on his skins in order to obtain a good glazed finish. Nevertheless, he has been willing to compromise and has begun to use nigrosine or diamine black for a part of his logwood, because he finds that iron or similar salts will bring up a harsh grain if not used with the greatest care. Some manufacturers are now using logwood without any striker and using enough diamine black to black the skins. Much less black would be required if no logwood was used, as the logwood forms a kind of resist for the diamine black.

Golden Brown Glazed Kid is most successfully made by dyeing with acid colors on top of a vegetable bottom.

The skins are first carefully washed and neutralized. Then they are bottomed 20 minutes in a coloring drum with 2% fustic extract, $\frac{1}{8}\%$ logwood crystals.

Then $\frac{3}{4}\%$ of a mixture composed of the proper proportions, anthracene yellow C or milling yellow O, orange extra, fast red B, naphthol blue black is added to the liquor in the drum and the skins are milled in it 30 minutes.

The skins are then drained off and vat-liquored either with acid vat-liquor or an emulsion of neatsfoot oil and egg yolk.

These colors penetrate deeply the skins and dye very level so that bright level shades are produced by glazing.

These colors are changed somewhat by the vat-liquor but are fairly fast to light.

The acid colors are sometimes topped with basic colors which makes the color much faster to fat-liquor.

Chrome Tanned Side Leather in tan, chocolate and green shades for sporting shoes is in considerable demand. They are usually neutralized and then given a retanning of 5 per cent sumac extract, $\frac{1}{4}$ per cent tartar emetic and 2 per cent acid fat-liquor, and dried on hooks.

Then the skins are sorted for the different shades, wet up and sometimes retanned with 5 per cent. fustic or sumac extract, then dyed with $\frac{1}{2}$ to 1 per cent. of a mixture of diamond phosphine G G, diamond phosphine R, bismark brown E E, cerise N, solid green O crystals.

These colors will produce any of the tan, brown, ox blood or green shades into which this kind of leather is made.

Then the color is sometimes fixed with $\frac{1}{8}$ per cent. of bichromate of potash and vat-liquored with 4 per cent acid vat-liquor.

The same shades can be successfully obtained with colors fast to light, as milling yellow O, diamine fast orange E G, brilliant croceine A Z, alizarine cyanole E F, naphthol green B.

Vegetable Tanned Leathers are usually colored with basic colors, except very light pearl and ecru shades which can be dyed better with easily levelling acid dyes. The principal difference in treating the different kinds of vegetable tanned leathers, is made in the method of preparation for coloring. The dyeing operations should be carried on at about 110° F.

India tanned sheep and goat skins contain considerable grease as well as vegetable tanning material. The grease must be removed from the surface of the leather before it can be dyed a clear, even color. This is done by washing the skins first in soda to free the grease; then retanning with sumac; then clearing with sulphuric acid; and finally the skins are rinsed with plenty of water. The skins are then colored with basic or acid dyes. The skins, to be colored black on the grain with white backs, are stained by brushing with 8 oz. leather black T B, 2 oz. acetic acid, and 2 quarts gum tragacanth solution, to 1 pail water.

Pickled sheepskins, tanned in sumac, are simply cleared with sulphuric acid and rinsed in water. Pickled sheepskins, tanned in quebracho, for fancy colors, are washed up in sumac, which is then fixed with tartar emetic.

India sheep and pickled sheepskins are colored similarly with acid and basic dyes, and can be considered together. Whenever good fastness to washing is required, the skins should be colored with basic dyes and the color set with bichromate of potash. On very light shades which must be slightly saddened, bichromate of potash should be used instead of blue or green, when possible. When full shades are made with acid dyes, such as bright reds, dyed with scarlet E C or brilliant crocein M O O, about 2 quarts of formic acid to 30 dozen skins should be added towards the end of the dyeing operation. Formic acid is generally chosen because it is quite as strong as sulphuric acid and will evaporate, while sulphuric is absolutely stable.

Dyes for ooze leather should be selected for their penetrating power.

Excellent results in coloring sheepskins can be obtained by dyeing first with acid colors, as, for example, dyeing coffee shades, first with Indian yellow G; tan shades, first with orange extra; and red brown shades, first with fast brown B N, and then topping with the proper mixture of diamond phosphine 2995 J, bismark brown E E, methylene blue B B or new blue R.

The acid dyes produce an excellently level bottom for the basic dyes.

Light pearl, gray, champagne, blue and heliotrope, are most successfully obtained by easily leveling dyes, such as cyanole fast green G, cyanole F F, lanafuch-sine S G and S B, orange extra, acid yellow A T.

These dyes also give good fastness to light.

Side Leathers for Case, Bag, Strap or Shoe Leathers are most satisfactorily dyed with basic dyes. The leather is usually bark tanned. Before coloring the leather is washed in water. About 30 sides are then

milled in 1 pail dry sumac for 20 minutes, and then a solution of 8 oz. tartar emetic is added and the sides milled 15 minutes longer. The skins are then drained off ready for coloring. Any of the tan, brown, Russia red and green shades can be obtained by a combination of diamond phosphine G G, diamond phosphine R, bismark brown E E, solid green O crystals, cerise N.

For light shades 1 oz. of dyestuff to 3 sides is sufficient; for dark shades 1 oz. to a side.

After dyeing, the color should be fixed with 5 to 10 oz. bichromate of potash. This prevents the color from stripping in the vat-liquor or in an alkaline finish.

Buffed Board Tanned Sides for shoe leather are usually colored with basic dyes. When the shoemaker uses this leather, he dips it into water to soften it. Basic dyes resist the water perfectly, but acid and other dyes wash off completely.

This leather is colored on only one side, and is therefore colored on a table by hand or in a brushing machine. As basic dyes are used, coloring with a machine is not very satisfactory because the brush, which spreads the dye, also whips it and makes it foamy. Then the dye does not work evenly. It is therefore better to brush it on by hand.

The color is often mixed with gum tragacanth or some similar gum to prevent the leather from absorbing the dye too rapidly. Some tanners mix soap and glue with the dye to save the operation of seasoning afterwards, but the soap throws the dye out of solution in a few minutes, so that it is impossible to get uniform results. The season should be applied after the skins are colored.

The Shell Oil Co., of London, England, is about to establish an oil refinery at Longue Pointe, near Montreal, Canada. Crude oil will be brought from Africa and refined at Longue Pointe.

A contract has been entered into between the Government of Venezuela and Dr. Rafael Max Valladares, representing the New York & Bermudez Co., authorizing Dr. Valladares to transfer the concession to the Caribbean Petroleum Co., which is organized under the auspices of the New York & Bermudez Co., an American corporation.

In its work of classifying and valuing the public coal lands the United States Geological Survey during January acted on nearly 3,000,000 acres of land which had been included in coal land withdrawals. Of this area 2,833,306 acres were classified as noncoal land and thus restored to public entry and 240 acres were appraised as coal land. Withdrawals of coal land were also made in Utah to the extent of 57,600 acres. There remains withdrawn, awaiting classification at the present time, 69,849,861 acres.

DETERIORATION AND SPONTANEOUS HEATING OF DIFFERENT COALS IN STORAGE.*

By HORACE C. PORTER and F. K. OVITZ.†

Not many years ago coal was commonly regarded as an extremely unstable material, subject to serious alteration and losses on exposure to the elements. E. C. Pechin, in 1872, speaking before the American Institute of Mining Engineers, says:

"Fuel suffers materially by * * * storage; especially with bituminous and semi-bituminous coals is the loss heavy, an exposure of only two weeks causing a loss of carbon to the extent of 10 to 25 per cent."

Similar views have been held in much more recent times. For example, in a paper before the United States Naval Institute, in 1906, we find the statement:

"The pressure of the weight of coal causes gases to be evolved; * * * these gases constitute the chief and only value of the coal, in that they furnish the heat units. It is claimed that if a ton of fine bituminous coal be spread out on a concrete pavement * * * in the open air in this climate—Key West, Florida—for one year it will lose all its calorific properties. The gases are simply free to escape, and when the coal has lost all its gas it will have lost all its heat units and be simply coke."

This was only five years ago; but in 1907 a German gas works engineer claims to have found that moist fine coal sustained an average loss per week of 1.7 per cent, this loss being due to gas. The 1889 edition of Groves & Thorp's "Chemical Technology of Fuels" says: "In some places coal is known to lose 50 per cent of its heating value in six months." Similar statements are to be found in recent literature; but probably the majority of chemists and engineers today hold no such exaggerated ideas on the subject. There is, on the other hand, a well-defined suspicion in the minds of many that sufficient loss of volatile matter, and sufficient deterioration by oxidation, does occur in coal to be of industrial importance; and for that reason the investigations described in this paper were undertaken by the Bureau of Mines to accurately determine the extent of the deterioration in different types of coal.

First, a study was made in the laboratory of the loss of volatile matter from crushed coal during storage. A number of samples—20 lbs. each—representing a variety of types from widely separated fields were broken to about ½-inch size and immediately placed in glass bottles in the mine. At the laboratory the accumulated gas was withdrawn, and a free continuous escape of the volatile products permitted at atmospheric pressure and temperature. The results of these experiments have been published in Technical Paper No. 2, Bureau of Mines, entitled "The Escape

*A paper presented by permission of the Director Bureau of Mines, at a joint meeting of the New York Sections of the American Chemical Society, American Electrochemical Society, and the Society of Chemical Industry, Nov. 10, 1911.

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of Gas from Coal," and will therefore not be given here in detail. It is sufficient to say that while several coals evolve methane in large volumes, especially in the early period after mining, the coal suffered in one year a loss in calorific value from this cause of but 0.16 per cent, as a maximum.

It seems, therefore, that the loss due to escape of volatile matter from coal has been greatly overestimated.

At the instance of the Navy Department, which is a purchaser of coal to the value of \$2,000,000 or \$3,000,000 annually, and which stores large lots in warm climates for long periods of time, elaborate tests were undertaken to determine the total loss possible in high grade coal by weathering. The extent of the saving to be accomplished by water submergence as compared to open air storage, was a point to be settled, and there had also arisen the question as to whether salt water possesses any particular advantage over fresh water for this purpose. An English railway and dock superintendent, in an article in the London "Engineer," 1903, reports that he has found coal accidentally submerged for 10 years in the salt mud of the English channel actually improved in calorific value by 1.8 per cent, "which offers a very pretty question to chemists to say why." He claims that salt will preserve the virtues of coal, as it does those of many other things; "If coal is given a strong dose of coarse salt and water 12 hours before using, its calorific value is greatly improved."

Coal storage problems have assumed importance during the last few years on account of the uncertainties of supply due to strikes and transportation difficulties. The naval coaling stations, the Panama Railroad Company, the Great Lakes commercial coal distributing companies, large coke and gas or power plants at a distance from the coal fields, and the railroads themselves, particularly those in the west, keep 50,000 to 500,000 tons in storage a great deal of the time. In brief outline, the tests by the Bureau were carried out as follows: Four kinds of coal were chosen, New River, on account of its large use by the navy; Pocahontas, as a widely used steaming and coking coal in the eastern section and as being the principal fuel used in the Panama canal work; Pittsburgh coal as a type of rich coking and gas coal; and Sheridan, Wyoming, sub-bituminous, or "black lignite"—a type much used in the west. Of the New River coal 50-pound portions were made up out of one large lot which had been crushed to $\frac{1}{2}$ -inch size and well mixed. These portions were confined in perforated wooden boxes and submerged under sea water at three navy yards differing widely from each other in climatic conditions, and 300-lb. portions from the same original lot were exposed to the open air, both out of doors and indoors, at the same places.

With the Pocahontas coal the test was made only on the Isthmus of Panama, run-of-mine coal being placed in a 120-ton pile exposed to the weather. Pitts-

burgh coal was stored as run-of-mine in open outdoor bins of five tons' capacity at Ann Arbor, Michigan, also in 300-lb. barrels submerged under fresh water. The Wyoming sub-bituminous was stored at Sheridan, both as run-of-mine and slack, in outdoor bins holding three to six tons each.

Every test portion was sampled each time in duplicate, and in all cases, except the outdoor pile at Panama and the 300-lb. open-air piles of New River, the sampling was done by rehandling the entire amount. In the excepted cases it was not thought fair to disturb the entire lot, and at Panama a vertical section of 10 tons only was removed each time, eight samples being taken from the 10-ton section. In the case of the outdoor lots at the navy yards a number of small portions, well distributed, were taken from each pile, mixed and quartered down.

Small lots and a fine state of division were conditions purposely adopted with the New River coal, so as to make the tests of maximum severity.

Moisture, ash, sulphur, and calorific value determinations were made on each sample, the latter by means of the Mahler bomb-calorimeter and a carefully calibrated Beckman thermometer. The calorimetric work on all except the Sheridan, Wyo., tests has been done throughout by one man, Mr. Ovitz, and with the same instrument. All the calorific values in the tables have been calculated to a comparable unit basis, viz. that of the actual coal substance free of moisture, sulphur, and corrected ash.

The results show, in the case of the New River coal, less than 1 per cent loss of calorific value in one year by weathering in the open. There was practically no loss at all in the submerged samples, and fresh water seemed to "preserve the virtues" of the coal as well as salt water. There was almost no slackening of lump in the run-of-mine samples, and the crushed coal in all cases deteriorated more rapidly than run-of-mine.

The Pocahontas run-of-mine, in a 120-ton pile on the Isthmus of Panama, lost during one year's outdoor weathering less than 0.4 per cent in heating value, and suffered little or no physical deterioration of lumps.

The Pittsburgh gas-coal, during six months' outdoor exposure, suffered no loss whatever of calorific value measurable by the calorimetric method used, not even in the upper surface layer of the bins.

The Wyoming coal lost as much as 5.3 per cent in one of the bins during two and three-quarter years, and 3.5 per cent in the first three months. There was bad slacking and crumbling of the lumps on the surface of the piles, but where the surface was fully exposed to the weather this slackening did not penetrate more than 12 to 18 inches in the $2\frac{3}{4}$ years period.

No outdoor weathering tests have been made by the Bureau on coal of the Illinois type. Thorough tests, however, on this type, have been reported by Prof. S. W. Parr, of the University of Illinois, and by A. Bement, of Chicago, both of whom find from 1.0 to 3.0 per cent calorific loss in a year by weathering. Mr.

Bement reports a slacking of lumps—in tests on small samples—of over 80 per cent in one case, and about 12 per cent in another. It is probable that in this type, as in the Wyoming coal, the slacking in a large pile would not penetrate far from the surface.

Storage under water unquestionably preserves the heating value and the physical strength of coal; but it practically necessitates firing wet coal, therefore means evaporating in the furnace an amount of moisture varying from 1 per cent to 15 per cent, according to the kind of coal. This factor is an important drawback to underwater storage with coals like the Illinois and Wyoming types, which, mechanically, retain 5-15 per cent of water after draining; but in the case of the high-grade eastern coals, if firemen are permitted, as is ordinarily the case, to wet down their coal before firing, "so as to make," as they say, "a hotter fire," the addition during storage of the 2 or 3 per cent moisture which these coals retain would be of little consequence. Submergence storage is an absolute preventive of spontaneous combustion, and on that account its use may be justified with some coals; but, merely for the sake of the saving to be secured by avoidance of weathering, there does not seem to be good ground for its use.

Losses in coal due to spontaneous heating are a much more serious matter. Oxidation—i. e., probably in the main an absorption of oxygen by the unsaturated chemical compounds in the coal substance—begins at ordinary temperature in any coal, attacking the surfaces of the particles and slowly developing heat. In a small mass of coal this slowly developed heat can readily dissipate itself by radiation, and no rise in temperature results. If radiation is restricted, as in a large pile densely packed, the temperature slowly rises. The curve of oxidation rate platted against temperature rises with great rapidity, and when the storage conditions are such as to allow a certain point—near 100° C.—to be passed, the rate of oxidation is great enough, ordinarily, so that the heat developed overbalances the heat radiated, and the temperature will rise to the ignition point if the air supply is adequate. The importance of guarding against even moderate heating in the coal, either from internal spontaneous causes or by radiation from external sources, can therefore be seen. Increased loss of heating value and of volatile matter occurs at moderately increased temperatures, even though the ignition point is not reached.

The amount of surface exposed to oxidation in a given mass depends on the size of the particles, and increases rapidly as the fineness approaches that of dust. Dust is, therefore, a dangerous thing in a coal pile, particularly if it is mixed with larger sized coal, which forms air passages to the interior. Spontaneous combustion is brought about by slow oxidation in an air supply sufficient to support the oxidation, but insufficient to carry away all the heat formed. There is a wide variation among coals in friability. In comparative rattler tests, under certain standard conditions,

Pocahontas, New River and Cambria county, Pa., coals produced nearly twice as much dust—through $\frac{1}{8}$ -inch screen—as a sample from the Pittsburgh seam. This is a large factor in spontaneous combustion. Mixed lump and fine—i. e., run-of-mine with a large percentage of dust—piled so as to admit to the interior a limited supply of air make ideal conditions for spontaneous heating.

High volatile matter does not, of itself, increase the liability to spontaneous heating. A recent circular letter of inquiry on spontaneous combustion sent by the Bureau to more than 2,000 large coal consumers of the United States has brought 1,200 replies, of which 260 report instances of spontaneous combustion, 220 of them naming the coal. Of these 220, 95 are in semi-bituminous low-volatile coals of the Appalachian region, and 55 in western and middle-western coals. This result at least shows no falling behind on the part of the "smokeless" type, and no cause for placing special confidence in these coals for safety in storage.

A serious fire in cinder-filling under a manufacturing plant in Pittsburgh was recently investigated by the Bureau, and all the evidence pointed to spontaneous combustion as the cause, induced by external heat radiated from a furnace. The cinders contained 40 per cent of carbon. A similar fire occurred two years ago in cinder-filling under a smelting plant on Staten Island, in which case the cinders contained 33 per cent carbon. Damage amounting to \$20,000 was done. The cause was not definitely determined, but, from the reports of the insurance adjusters, spontaneous heating appears to be the most plausible explanation. The volatile matter in the material could not have been a factor in these causes.

Pocahontas coal gives a great deal of trouble with spontaneous fires in the large storage piles at Panama. It is reported also by several large by-product coke concerns to be more troublesome in this respect than their volatile gas coals. The high volatile coals of the west are usually liable to spontaneous heating, but they owe this property to the chemical nature of the substances which compose the coal rather than to the amount of volatile matter. Strange as it may seem, a high oxygen content in coal appears to parallel its avidity for oxygen and to promote, therefore, its tendency to spontaneous combustion.

The influence of moisture and of sulphur upon spontaneous heating of coal are mooted questions much discussed, but not very much actually investigated, and certainly not yet settled. Richters has shown that in the laboratory dry coal oxidizes more rapidly than moist, but the weight of opinion among practical users of coal is that moisture promotes spontaneous heating. The observation by the Bureau of many actual cases has not developed any instances where moisture could be proved to have had such an effect. Sulphur has been shown by these investigations to have, in most cases, only a minor influence. In a number of cases samples of heated coal from areas where the heat

was greatest have been analyzed, both for total sulphur and between these, in other words the unoxidized sulphur, was in no case less than 75 per cent of the average total sulphur in the original. In other words, not more than $\frac{1}{4}$ of the total sulphur has entered into any heat-producing reaction. The possibility remains, however, that all of the sulphur which was oxidized was concentrated in one pocket of moist, flaky pyrites, and thus sufficient heat was developed in one spot to act as an igniter. On the other hand, a Boston company, using Nova Scotia coal of 3 to 4 per cent sulphur, has much trouble with spontaneous fires in storage, but a number of samples taken by the Bureau from exposed piles of this coal in which heating had occurred showed that 90 per cent of the sulphur was still unoxidized. Experiments in the laboratory in passing air over coal at 120° C. have developed enough heat to ignite the coal, and no change was found in the form of the sulphur. While not entirely conclusive, these results point to a minor contribution, if any, on the part of sulphur to spontaneous heating in coal.

Freshly-mined coal, and even fresh surfaces exposed by crushing lump coal, exhibit a remarkable avidity for oxygen, but after a time become coated with oxidized material, "seasoned," as it were, so that the action of the air becomes much less vigorous. It is found, in practice, that if coal which has been stored for six weeks or two months, and has become already somewhat heated, be rehandled and thoroughly cooled by the air, spontaneous heating rarely begins again. A large power plant in New York crushes its coal to pass a 4-inch screen immediately after unloading from barges, the fines and dust, 50 per cent or more, being left in the coal to be stored. This freshly-crushed coal is elevated to iron hopper-shaped bunkers directly over the boilers, and the air temperature in these often reaches 100° F. As the coal hangs on the sloping sides, sometimes three or four months at a time, it seems hardly surprising that some of the bunkers are on fire practically all of the time.

With full appreciation of the fact that any or all of the following recommendations may, under certain conditions, be found impracticable, they are offered as being advisable precautions for safety in storing coal whenever their use does not involve an unreasonable expense:

1—Do not pile over 12 feet deep, nor so that any point in the interior will be over 10 feet from an air-cooled surface.

2—If possible, store only lump.

3—Keep dust out as much as possible; therefore reduce handling to a minimum.

4—Pile so that lump and fine are distributed as evenly as possible, not, as is often done, allowing lumps to roll down from a peak and form air passages at the bottom.

5—Rehandle and screen after two months.

6—Keep away external sources of heat; even though moderate in degree.

7—Allow six weeks' "seasoning" after mining before storing.

8—Avoid alternate wetting and drying.

9—Avoid admission of air to interior of objects, such as timbers or irregular pile through interstices around foreign brick work; also through porous bottoms, such as coarse cinders.

10—Do not try to ventilate by pipes, as more harm is often done than good.

The much discussed waste of natural gas is stated by the United States Geological Survey to be rapidly decreasing. The problem of conserving the natural gas supply may be considered as having been satisfactorily solved in Pennsylvania, throughout the Appalachian and the Lima-Indiana fields, and in Kansas. The greatest waste is in Oklahoma and in the Caddo field of Louisiana, owing in Oklahoma to probable looseness in enforcement of the laws and in Louisiana to lack of a market. It is noteworthy that one of the two wild wells in Louisiana that have been sensational examples of waste have been successfully closed and the gas thus conserved for future use.

Plans for the development of the steel making industry in South Africa are well advanced. Announcement has been made that two new mills are to be erected, and the following additional enterprise as described in the London Times shows the prospective rapid growth of the new industry: The formation of the Union Steel Corporation (of South Africa) (Ltd.), marks an interesting stage in the industrial progress of South Africa. It is proposed to establish iron and steel works and rolling mills at Vereeniging in the Transvaal, and the company is already assured of influential support. The Government of the Union of South Africa has entered into an agreement with a director of the company (which is transferred to the company) whereby the corporation acquires the preferential right to purchase iron and steel scrap from the Government railways and shops for 16 years, at £1 (\$4.86) per ton, for the whole of the Transvaal, and a large district south of it, and at satisfactory prices for the remainder of South Africa. The Government has also agreed during the same period to increase the railway rates on exported scrap and to grant the corporation a reduced rate for transport of their scrap to the corporation's works, and also to place their orders for such iron and steel goods as the corporation produces with the corporation. The agreement provides that the company shall erect and install the necessary works for the business, and take delivery of the scrap within the times provided by the agreement. The company is also required after the third year of its beginning manufacture to make certain experiments in smelting, working, and treatment of local iron ores.

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NOTES AND COMMENTS.

National Bureau of Standards.

It is the opinion of the writer that the work of the National Bureau of Standards is only partially understood by the chemists of this country. Probably all of us are familiar with the fact that the Bureau of Standards prepares analyzed samples of various metallurgical products, calibrates thermometers, glass measuring apparatus, etc. It is probably true, however, that the broader and perhaps more important work of the bureau is little understood by the person who has not been brought in actual contact with its operations in various lines of industry.

This broader field of work covers a line of operations in keeping with its name, and which will be of fundamental importance to scientists, particularly to the chemists and chemical engineers of this country. It appeared to the writer that the ideal of this bureau is to make it in practice what its name implies: a bureau of standards. This does not mean a bureau of standards for weights, measures, electrical units, units of time, etc., but while meaning this, also has a much broader meaning which is now being emphasized by the labors of the men in this department, and as an illustration of this, one might cite their work on paper.

The government is a very large purchaser of paper of various kinds, weights and qualities. It was a matter of fundamental importance to draw a specification

which would properly cover the purchase of grades of paper satisfactorily for the various purposes desired. So little information was available along these lines that a small paper machine has been installed, and experiments will be made to determine just what composition and method of treatment will be required to obtain a paper such as is desired for the various purposes. Such information will then be embodied in a specification drawn to cover the purchase of this material.

Work is also being done along other lines which are interesting to the chemical engineer, such as the development of standard methods for testing rubber and rubber goods; standard methods and standard apparatus for testing lubricating oils, particularly in the determination of their viscosities.

Much work is also being done in comparing types of calorimeters, both for solid and liquid fuels. Suggestions will be ultimately made indicating types of calorimeters most suitable for various purposes.

A large amount of work has already been done in the study of various pyrometers of all kinds. This work is being continued, and has done much towards evolving typical pyrometers which are satisfactory for all kinds of heat measurements.

The bureau also has under consideration, and in time will probably take up the definition and specification covering the composition of various industrial products, such as alloys, etc. In fact, it seems to be the desire of responsible heads of the bureau to act in fact, as well as in name, as a bureau of standards, to which will be referred many of our industrial questions, which at present are only vaguely understood because the conception of them has been limited to that, loosely formulated in trade practice or trade custom.

Potash Dispute Finally Settled.

We have abstracted the following from the *Oil, Paint and Drug Reporter*:

The official announcement has been made at last that the potash controversy between the consumers in this country and the German Government backing the Kali Syndicate has been settled. It is announced that the last of the contracts compromising the dispute were signed and delivered during the last week in December. The terms upon which the settlement or settlements were effected have not been made public, and probably never will be. The American consumers were paid lump sums to surrender their contracts, but from these sums were deducted the amounts that had to be refunded to the independent mines for the cancellations of their American contracts.

The result of this settlement appears to be a victory for Germany and a failure on the part of American consumers to secure potash at a figure somewhere near the cost of production. It also means that the German monopoly in potash is made absolute and that those who use this chemical must expect to pay whatever price the Imperial government demands. In

addition it means that the independent mines are again allied with the official potash syndicate and that hereafter there will be no competition which can be of any benefit to the consumer. This is a method of conducting business which is practically unknown in this country, where corporations and trusts are being vigorously denounced and punished. Such a thing as the fostering of an official trust which will pay a revenue to the government, and will sell its products at an enormous profit, has not as yet been proposed in America. As long as the German government maintains its control it will have the entire trade within its grasp. It is not likely, however, that after the lesson which they have just received the Americans will again attempt to make contracts which are not officially authorized.

One result of the controversy has been to stimulate into greater activity the efforts of the United States government to discover potash resources in this country. These efforts will continue as the present terms of settlement with the Germans are not sufficiently alluring to be maintained except as a matter of necessity. In another column of the present issue will be found a history of the negotiations which have resulted in the settlement, as well as of the various efforts made in this country to discover potash and a discussion on the possibility of success. It must be admitted that the latter are not very favorable and that the experts of the government practically admit that except for the recovery of potash from the kelp seaweed, which abounds on the Pacific coast, there is little immediate prospect of sufficient quantities being secured to relieve our consumers from the thralldom of the German monopoly.

BOOKS RECENTLY RECEIVED.

Applied Electrochemistry. — By M. DeKay Thompson, Ph. D. The Macmillan Company, New York, 1911.

This is the only book in English that attempts to cover the whole field of electrochemistry. The subject is so big that any attempt to cover it in the scope of a single volume must result in a more or less superficial treatment of a large part of the material. The question of emphasis in such a subject will have as many answers as there are authors. So that if parts of the field have been merely mentioned, if some parts have been emphasized more or less than the reader thinks proper, it should be taken as a natural result of the intention of the author to collect "in a single volume the material that would be comprised in a course aiming to give an account of the most important electrochemical industries, as well as the principal applications of electrochemistry in the laboratory."

The book is an excellent one both in conception and execution. The reviewer hopes the author and publisher will revise it regularly and frequently to keep it abreast of the rapidly developing subject.

The Chemistry of the Coal-Tar Dyes.—By Irving W. Fay, Ph. D. (Berlin). The D. Van Nostrand Co., New York, 1911.

This book, in the words of the author, is intended for those students and dyers who have a good knowledge of general chemistry, and some knowledge of organic chemistry.

The origin of the coal-tar dyes is first described; then the production of coal-tar and its products. The essentials of what is usually included in a study of the aromatic division of organic chemistry is described in two chapters of fifty pages. Then the nitro and nitroso dyes, the triphenylmethane dyes, the azo dyes, the pyronines, the indamines and their derivatives, the eurhodines and their derivatives, the quinoxalines, aniline black, the alizarin dyestuffs, indigo and the sulphur dyes are described in turn.

The methods of preparing the dyes are described, and the group and individual relationships are shown. The development of one color from another by changing the composition of the dye is explained.

There is a chapter on mordants, also a valuable chapter on "the seven food colors." Forty pages of experimental work are given.

The reviewer believes that much more than "some knowledge of organic chemistry" is necessary for a comprehension of the chemistry of the subject, so well developed by the author. The reviewer values the book highly as a contribution to the already extensive literature of the dyestuffs. The publishers deserve much praise, especially for the clear-cut way in which the complicated structural formulae are represented, and for the general appearance of the book.

Technical Methods of Chemical Analysis.—Lunge. Vol. 11, Parts 1 and 2. D. Van Nostrand Co. Price, \$18.00.

This book contains most of the methods of technical analysis in common use, and in addition to this there is much descriptive matter relating to the materials to which the analysis is to be applied. A most excellent feature of the work is that the methods of analysis described have given also the place where they are used or the individual who uses them. It would be possible for a chemist to carry on practically all of his technical analysis if he had no other book than this to which he could refer. It can be very highly commended to the analyst who wishes to have in his library a book covering a wide range of subjects and at the same time one which is accurate and concise in its statements on the methods to be employed in an analysis.

Rubber, Its Production and Its Manufacture.—By Phillip Schidrowitz. D. Van Nostrand Co. Price, \$5.00.

A book which appears to be a most excellent presentation, of the production, treatment and uses of rubber. The descriptive matter throughout is most excellent. The illustrations are all that could be desired.

It has been long since a book has appeared which shows better preparation and presswork than this one. We can commend it to those interested in any part of the rubber industry.

Qualitative Analysis.—By J. I. D. Himbs. Chemical Publishing Co.

I find in this text-book, one of the more recent ones of its kind, a good discussion of the methods of qualitative analysis as based on the theories of solution and of electrolytic disassociation.

Technical Analysis of Brass.—By Price & Meade. John Wiley & Sons.

This book is more than its title indicates, as it includes a description of the various engineering alloys in use and then gives a description of the methods applicable to the determination of the metals commonly present in such alloys. The book could be criticized from the point of proper selection of methods. Some excellent methods are given, usually one of each which is satisfactory for the metals which are under discussion. There are, however, included many methods which should never have found place in a book of this character, as for example, electrolytic methods for the determination of aluminum, iron, antimony, manganese, etc. It seems to be the authors' intention to give the method, if it has been described at all in the literature, whether it worked out satisfactorily or not.

The book contains much valuable material on methods of analysis, but would be much more valuable if faulty methods were discarded, and only those methods which have been found satisfactory in practice included.

Qualitative Analysis.—By Arthur E. Hill. Chemical Publishing Co. Price, \$1.00.

It has been the writer's opinion that every chemist thinks that at some time he must write a book. Most chemists start by writing a qualitative analysis. This book seems to be such a product, and I can see nothing new in it either in the method of procedure given or in the theory advanced.

Fertility and Fertilizer Hints.—By Jas. E. Halligan. Chemical Publishing Co. Price, \$1.25.

This book contains a discussion of the chemical elements needed by plants, the items which enter into the fertility of the soil and means which may be adopted for maintaining such fertility. A discussion is then given of the various fertilizers on the market, together with their ingredients. A chapter is also given on the valuation of fertilizers, and one on the home mixing of fertilizers. It is a valuable book for anyone connected with the pursuit of agriculture or in the manufacture of fertilizers.

Portland Cement.—By Richard K. Meade. Chemical Publishing Co. Price, \$3.50.

The author of this work on Portland cement is well known for the work he has done along this line. The second edition of his book, which is noted here, gives a description of all of the operations connected with the manufacture of Portland cement. It also gives a

very complete description and discussion of the chemistry involved in the process. The standard methods for testing cement are given as well as the standard specifications for cement and cement materials. The book is one which should be in the hands of all persons connected with the cement industry.

Metallurgy of Iron and Steel.—By Bradley & Stoughton. McGraw-Hill Co. Price, \$3.00.

The second edition of this book is now on the market. The text-book has been brought up to date, quite a little additional material has been added, and some of the mistakes of the earlier edition have been corrected. As the book stands today, it is one of the best text-books we have on the metallurgy of iron and steel.

Contemporary Chemistry.—E. E. Fournier D'Albe. D. Van Nostrand Co. Price, \$1.25.

This little book attempts to give a bird's-eye view of the whole field of modern chemistry. Each discussion is carried down to 1910. Physical chemistry and physical and electrical theories of chemical phenomena predominate. The book is almost a chemical physics. It is very readable, and it is up-to-date.

B. B. FREUND.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of patents, McGill Building, 908 G street, N. W., Washington:

- 1,010,490. Method of Reducing Ores. Otto Frick, Stockholm, Sweden. Patented December 5, 1911.
- 1,011,014. Process of Manufacturing Oxides of Nitrogen. Oscar Bender, Potsdam, Germany. Patented December 5, 1911.
- 1,011,043. Process of Making Ammonium Sulphate and Sulphur from Gas. Walther Feld, Linz, Germany. Patented December 5, 1911.
- 1,011,172. Process of Obtaining Potash from Green Sand. Edwin C. Eckel, Washington, D. C. Patented December 12, 1911.
- 1,011,173. Process of Producing Metallic Iron and Alkaline Salts. Edwin C. Eckel, Washington, D. C. Patented December 12, 1911.
- 1,011,238. Explosive. Gershom Moore Peters, Cincinnati, and Milton Fletcher Lindsley, Kings Mills, Ohio, assignors to the King Powder Company, Cincinnati, Ohio, a corporation of Ohio.

This explosive is composed of nitrate of ammonia, nitrate of soda, chlorate of potassium, mirbane oil and a carbonaceous material capable of being easily inflamed, mixed together into a mass.

- 1,011,659. Manufacture of Varnishes. Edward Halford Strange, Staple Inn, London, England, assignor of one-half to Edmund Risolieri Burrell, Millwall, London, England. Patented December 12, 1911.

This is a process of manufacturing varnish which comprises the step of dissolving copal by heating the latter under pressure, but not materially in excess of 250 pounds to the square inch, in the presence of a quantity of a volatile solvent less than required in the finished product.

- 1,011,897. Treatment of Complex Ores. Edgar Arthur Ashcroft, Sogn, Norway. Patented December 19, 1911.

This is a process of separating metals from zinc sul-

phide containing other metallic sulphides, which consists in the reaction of zinc chloride with said metallic sulphides in the fused state to precipitate zinc sulphide and dissolve the other metals, pouring off the liquid melt consisting of zinc chloride having in solution chlorides of the other metals from the solid residue to separate the melt from the residual zinc sulphide, and thereafter treating the melt to recover the metals therefrom.

1,012,310. **Manufacture of Iron and Steel.** Frank A. Wilmot, Bridgeport, Conn. Patented December 19, 1911.

1,012,368. **Explosive Compound.** George G. King and Milton F. Lindsley, Deerfield township, Warren county, Ohio; said Lindsley assignor to said King. Patented December 19, 1911.

The explosive comprises saltpeter, charcoal, nitro-cellulose, sulphur, nitro-starch, nitro-sugar, oil of mirbane and asphalt.

1,012,421. **Manufacture of Sulphuric Acid.** Carl Opl, Hruschau, Austria-Hungary, assignor to the firm of Erste Oesterreichische Sodafabrik, Hruschau, Austria-Hungary. Patented December 19, 1911.

The process consists in passing burner gases containing sulphur dioxide under pressure into a system of reaction towers and producing a rapid circulation of nitrous sulphuric acid through the system by feeding compressed burner gases and compressed air to the acid eggs to raise the nitrous sulphuric acid into the towers and to come into intimate contact with the said acid, whereby oxidation of the burner gases is effected.

1,012,467. **Process of Producing Cement and Products Thereof.** Arthur C. Spencer, Washington, D. C. Patented December 19, 1911.

This is a process of producing a cement and recovering zinc which comprises comminuting calcareous ore tailings carrying zinc oxide and zinc silicate, exposing such tailings to a sintering heat and collecting the clinker and furniform zinc oxide produced.

1,012,511. **Method of Detinning.** Heinrich Brandenburg, Kempen-on-the-Rhine, Germany. Patented December 19, 1911.

1,012,531. **Process for the Manufacture of Solid Fashioned Bodies Containing Silicon Carbide.** Georg Egly, Charlottenburg, Germany, assignor to Gebr. Siemens & Co., Charlottenburg, Germany. Patented December 19, 1911.

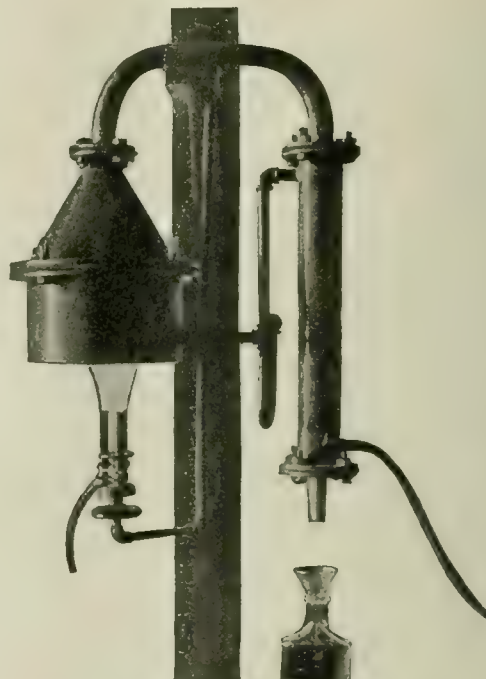
1,012,639. **Method of Quantitative Analysis of Solutions.** Israel Fritiofson Holmgren, Stockholm, Sweden. Patented December 26, 1911.

This is a method of determining the percentage of a substance in solution which consists in forming a scale upon unsized paper by means of an indicating medium which is adapted to change its color by influence of the substance which is to be determined, placing a small quantity of the solution upon a point of said scale and determining by means of said scale the ratio between the area of the central circular portion of the wet spot which has changed color and the area of the annular zone portion of the spot which has not changed color and which surrounds the said central portion.

1,012,665. **Process for Electroplating with Zinc.** Auguste Arsene Lemetre, Paris, France. Patented December 26, 1911.

1,012,676. **Briquet.** Charles T. Malcolmson, Chicago, Ill.

AUTOMATIC WATER STILL



A serviceable gas distilling apparatus.

Capacity 1-2 to 9-10 gallons per hour.

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THE EFFECT OF TEMPERATURE UPON DUCTILITY OF ZINC.*

By W. B. HAINES,[†] B. SC.

It is well known that zinc has the property of becoming soft at temperatures in the region of 150°C., while it is said to become hard and brittle at about 200°. This applies to the commercial variety of the metal, which always contains a small proportion of lead. These changes suggested an investigation into the effect of temperature upon the ductile properties of zinc, of which the present paper is a record.

The experimental plan adopted was the examination of the ductility of zinc wires at various temperatures. Wires about 15 cm. long were fixed in a vertical position in a bath of castor oil, and stretched by a weight applied to the upper end by means of a pulley. A cathetometer was used to measure the extension of the wire. At each particular temperature the rate of extension of the wire was calculated from the observations for several loads ranging up to the breaking stress.

The results of the work emphasize the importance of treating the wires in exactly the same manner in order to gain consistent results. Thus the state of the wire as indicated by the rate of extension under a given stress depends not only upon the temperature, but also upon other factors, such as the previous treatment which the wire has received. In order to gain the required consistency of result, the wires were prepared and used in the order of their position on the original bank of wire, so minimizing the effect of any variation in condition along the hank. An endeavor was also made in obtaining a set of readings from each wire to maintain uniformity of treatment in all respects. The method of taking the readings was largely determined by the requirement that the behavior of the wire should be investigated right up to the breaking point before an undue amount of stretching had introduced uncertain effects. This condition prevented the repetition of readings, which would otherwise have been desirable, as the flow of zinc was not uniform.

Expression of Results.—The result of each experi-

ment has been diagrammatically expressed by plotting the rate of extension per unit length R against the stress per unit¹ cross-sectional area S . Both R and S require a correction introduced by the stretch of the wire. In the calculation of R the mean length of the wire during the reading was used. The correction applied to S is made necessary by the diminution in diameter corresponding to the increase in length. It was made on the simple assumptions that the thinning is uniform, and that constant volume is maintained. Then, if s be the extension and e the original length, the ratio of the applied stress to the corrected stress S is $1:1 + s/e$. The suppositions involved here were tested by comparing measurements of the wires made

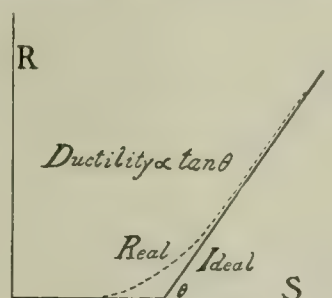


Fig. 1.

before and after the experiments upon them. The comparison showed that any irregularities in diameter were about doubled by the stretching, and that the correction as applied to S was reliable to 0.7 per cent. These measurements also showed that differences between the diameters of different wires were small enough to be neglected. No correction was made for the very small friction of the pulley.

In this manner a curve was obtained for each temperature chosen over a range from 10° to 200°C. The results have been brought together by taking as a measure of the ductility the slope of the final portion of the curve corresponding to the particular temperature. In the case of a truly viscous flow, R and S are connected by a linear law, or $dR/dS = k$, where k is a constant proportional to the coefficient of viscosity. With such substances as pitch, which while approximately viscous in behavior can yet be treated in the manner of the present experiments, k has been called the coefficient of viscous traction.² The behavior of the zinc has thus been assumed to become approxi-

[†]Physics Research Scholar, University College, London, England.

*From the Proceedings of the Royal Society.

¹For the sake of convenience the unit taken was the initial cross-sectional area = 0.00581 sq. c. m.

²Trouton, Royal Society Proceedings, A, Vol. 77, p. 426.

mately viscous toward the breaking stress. This assumption is justified by the results over a considerable range of temperature, and in any case the method gives a convenient and fairly accurate means of comparing the results. Fig. 1 gives a clear idea of what is involved in the assumption. In the ideal case an abrupt change from the elastic to the viscous state is supposed instead of the more gradual change which the real curve indicates.

Results.—A preliminary experiment was first made upon a single wire under a constant load, the rate of extension being measured at intervals as the temperature rose from 70° to 150°C. The result showed two notable changes in the zinc over this range. Between 80° and 90° the metal becomes remarkably soft, as soft, in fact, as it is at 150°. At a few degrees above 90° a very definite hardening sets in, which has a turning point at about 115°.

Curves covering the whole range of the experiments are shown in Fig. 2. These have been selected from a great number of perfectly consistent experiments, as being representative of the series. The experimental points have been omitted from all the curves save three, in order to avoid confusion. These three, together with the table, give a sufficient idea of the experimental data upon which the results are based. The diagram shows curves for intervals of 20° between 50° and 200°C., except between 90° and 120°, where the interval is reduced to 10°. Below 50° the stresses involved are too large for curves to be completed on this figure. An approximate idea of the behavior at atmospheric temperature can be gained by taking the curve marked 122° and doubling the abscissae.

TEMPERATURE, 108° C.

Load, kgm.	Extension per minute, cm.	Length of Wire, cm.	Rate of Extension, (corrected)	Street
3.0	0.032	16.2	0.0020	3.00
3.5	0.071	16.3	0.0045	3.52
4.0	0.121	16.4	0.0074	4.06
4.4	0.196	16.6	0.0118	4.51
4.6	0.246	16.8	0.0146	4.76
4.8	0.312	17.0	0.0184	5.03
5.0	0.368	17.2	0.0214	5.31

The state of the zinc at any particular temperature is indicated both by the shape of the curve and by the position of the curve upon the diagram. The three curves, 50°, 69° and 90°, show a regular increase in softness as the temperature rises, the form of the curves at the same time decreasing in curvature. At maximum softness the curve is practically a straight line, which indicates that a truly viscous behavior is reached. At a few degrees above 90° a hardening of the zinc sets in, which is so rapid that, at 110°, the behavior is comparable with that of 30°. There is, however, greater brittleness than at this lower temperature. From 110° onward there is a regular softening as the temperature rises. This certainly continues up to 200°, and one or two experiments above this temperature indicated that the softening continues at least up to 250°C. Although the zinc attains, at these higher temperatures, the same ductility as it shows at

90°, the character of the flow is different in the two cases. At the lower temperature, increase in softness corresponds to straightening of the curve, but at the higher temperature the reverse is the case, for a regular increase in curvature is noticed as the temperature rises. The contrast is clearly shown in Fig. 2 by the curves marked 90° and 180°. At 90° the wire can also be extended a greater amount, without breakage than is possible at higher temperatures.

It is worthy of note that the hardening of the zinc which occurs in the region of 100°, takes some time to develop. Thus the wire, immediately upon attaining this temperature, is soft, but after a short time it sets into a harder state. This fact was not at first appreciated, with the result that curves of the form shown in Fig. 3 were obtained for experiments between 90° and 100°. Since the readings were started directly

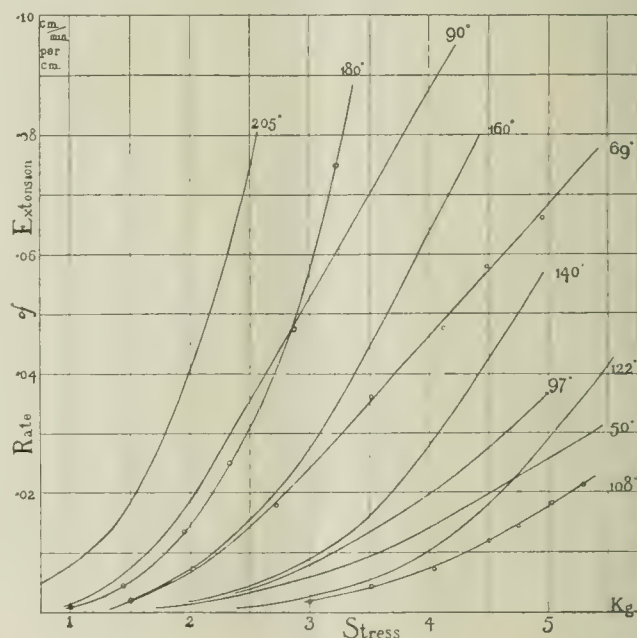


Fig. 2.

the wire was fixed in the bath, the time effect is superposed upon that due to changing the loads. This time lag was separately investigated by keeping the load constant. At 98° the rate of extension fell to one-eighth of its initial value during the first six minutes, at the end of which time the zinc had reached a permanent state. This effect of initial softening, followed by gradual hardening, is noticeable only between 90° and 120°. It is most definite at the beginning of this range, becoming smaller and more rapid towards the end.

The best representation of the results is to be found in Fig. 4, which shows the coefficient of ductility as calculated from each curve in the manner already explained, plotted against the temperature. It is interesting to note that the ductility, after a fairly definite change at 120°C., increases uniformly with rise in temperature. It was the discovery of this change at 120° which first showed, about a century ago, that zinc could be brought into a plastic state by simply heating it to a very moderate temperature. This simple fact

converted a little used metal into one finding extensive and valuable application in such trades as building. No previous notice, however, seems to have been taken of any peculiarity in the ductile properties of zinc at temperatures below 120° . Another noticeable feature of this diagram is that the softening which occurs toward 90° is as much a departure from the mean curve as is the hardening at 110° .

Discussion of Results.—The effect of the mode of

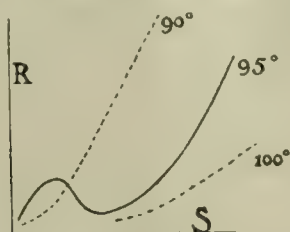


Fig. 3.

treatment of the zinc upon its behavior has already been mentioned. The effect of heating the wire to temperatures above 120° and then cooling, is to diminish greatly its tenacity and ductility. This is due to the crystalline structure induced, as is shown by a microscopical examination of the fracture, and the change affects the behavior at all temperatures when the wire is again heated. In this state the zinc does not show any of the peculiarities already explained. Its behavior is very erratic, but shows on the whole a gradual softening as the temperature rises. In order to restore the ductility to the zinc all that is needed is to subject it to some such mechanical process as hammering. This crushes out the coarse crystalline structure, rendering the metal homogenous and much more ductile. This was very marked in an experiment upon a small bar of zinc, which was hammered at a temper-

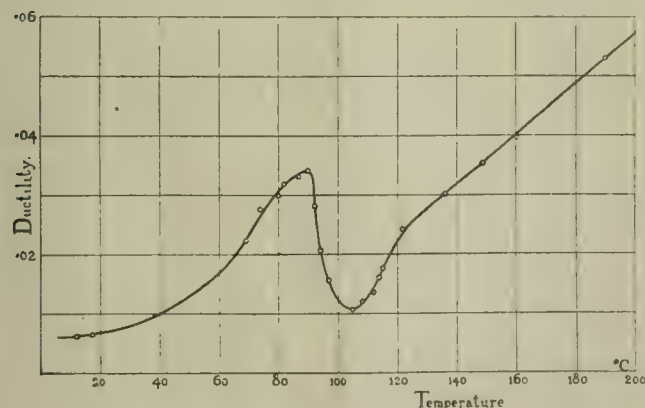


Fig. 4.

ature of about 150°C ., the test of its ductility being applied by flexure.

Considering how large is the number of factors which combine to determine the behavior of the wire, and hence the form of the curves by which this has been represented, it will be seen that the curves have by no means as simple a physical meaning as their appearance would suggest. This explains why an endeavor to find a simple mathematical expression for them was

not successful. More involved expressions could have been fitted, but their significance would be doubtful.

In all the experiments so far recorded ordinary commercial zinc was used, since this is the only kind obtainable in the form of wire. A careful analysis of the specimen used revealed the presence of 0.52 per cent lead. It was thought to be desirable to know whether the peculiarity in the behavior of this wire was due to the presence of lead, or to a true characteristic of zinc itself. The experiments could not be repeated with pure zinc, as it is impossible to produce wires of the pure metal. However, a comparison of the behavior of the two forms of metal was obtained by applying the method of flexure. A rectangular bar was sawn from a cast stick of pure zinc, and supported at either end in a small iron frame immersed in the oil bath. The precaution was taken of previously hammering this bar. Its rate of flexure under a force applied to its middle was then observed at different temperatures. In the case of commercial zinc a set of wires fixed side by side was substituted for the bar. These showed the same changes in the region of 100°C . as were observed in the experiments on stretching the wires, but, although these changes are so very marked, they could not be observed in the pure zinc. The bar showed a uniform softening as the temperature rose, the only peculiarity being a hardening in the region of 200° . Hence the evidence leads to the conclusion that the singularity observed in the ductility of zinc at temperature in the region of 100°C . is produced by the admixture of a small proportion of lead.

Charcoal is used to a considerable extent in Sheffield, one wholesale firm dealing in it estimating the aggregate amount handled at \$150,000 yearly, with a considerable quantity purchased by large firms direct from local burners. The manager of one large steel firm states its annual consumption at about \$2,500 bought direct. The price this firm pays is about 12 cts. per bushel, which at 14 lbs. to the bushel works out at \$19.20 per ton. The firm of dealers interviewed says it has in times past bought from various markets outside of Sheffield, but owing to the bulky nature of charcoal and the high freight rates it procures as much as possible of its supply from local burners. It has never bought from foreign producers. The price fluctuates somewhat, depending on supply and season. The average price (steel charcoal excepted) is \$15.81 per ton f. o. b. Sheffield. Three sizes of charcoal are sold—stick, steel, and powdered. The stick is made from small twigs, usually about three-fourths of an inch in diameter and from 5 to 6 ins. long. This is the kind most in use. Steel charcoal is in cubes and ranges in price about \$2.40 higher than stick.

Exports of flour from Canada amounted to \$10,015,778 in the eight months ended Nov. 30, 1911, one-half of the shipments going to the United Kingdom.

COKE OVEN TARS OF THE UNITED STATES

The rapidly increasing use in this country of refined coal tar in the treatment and construction of roads and the fact that an immense quantity of coal tar will ultimately become available for this purpose through the installation of by-product coke ovens make it highly desirable to obtain accurate information as to the properties of coke oven tars which are being produced at present. An investigation with this end in view has been conducted by Prevost Hubbard, chemist, U. S. Office of Public Roads. The results are set forth in a bulletin issued recently by that office, from which we have taken the matter that follows.

While in the manufacture of coal gas the production of tar is absolutely unavoidable, this is not true of the manufacture of coke for metallurgical purposes. There are two general types of coke ovens in use at present, in one of which no attempt is made to recover the volatile products of the coal. This is the oldest form of oven, known as the "beehive," and is extensively used in this country today. It is constructed of brick and as its name implies has the form of a beehive. Bituminous coal is placed in this oven or kiln and a part of it burned in order to carbonize the remainder, while the volatile products, such as gas, ammonia, and tar, are allowed to escape through an opening in the top of the kiln, where they are lost in flame and smoke.

Coke ovens in which the by-products are saved are now used to some extent in this country, and sooner or later will undoubtedly replace the old style oven entirely, and thus increase our output of tar enormously. The reason that they have not been more generally adopted in this country is that in the United States tars are of much less economic importance than in the European countries, where great chemical industries are based upon the utilization of this material. Germany in particular is far in advance of us in this field and exports to this country alone coal tar products to the value of several million dollars each year. With the development of the road tar industry, which promises to consume vast quantities of tar, and the necessity for refining such tars before use, the general adoption of by-product ovens is only a matter of time. What this will mean in the increase in tar production can be imagined from the fact that in 1908, out of a total of over 26,000,000 tons of coke produced in coke oven, only a little over 4,000,000 tons were obtained from by-product ovens. About 22,000,000 tons of coke were therefore produced without recovery of the tar. As the average yield of coke per ton of coal was 66 per cent, this would represent the consumption of over 33,000,000 tons of coal. Upon the basis of a yield of 10 gallons of tar per ton of coal, it may be seen that over 330,000,000 gallons of tar were lost in 1908 which might have been saved. As the actual production of coal tar both from coke ovens and gas houses amounted to about 101,000,000 gallons, it is evident that over three-fourths of our possible production of tar as a by-product was lost during that year. At a

valuation of $2\frac{1}{2}$ cents per gallon, this means a loss of over \$8,000,000. With such an increase in production, however, the monetary value of coal tar would have dropped, so that this figure may be somewhat exaggerated. In any event, at a conservative estimate, the tar lost each year from non-recovery coke ovens is sufficient to build 9,000 miles of tar macadam road 15 ft. wide.

This estimate was based on data taken from reports of the United States Geological Survey. In a later report by Parker¹ it is shown that over 53,000,000 tons of coal were consumed in beehive ovens in 1910, so that on the same basis it would appear that over 530,000,000 gallons of tar were lost during that year. The output of tar from by-product coke ovens, however, has also continued to increase, as shown by the following figures taken from this report:

TAR OBTAINED FROM BY-PRODUCT COKE OVENS.

	Gallons.
1908.....	42,720,609
1909.....	60,126,006
1910.....	66,303,214

The tar thus produced in 1910 was valued at \$1,599,453, or about 2.4 cents per gallon. It is evident therefore that the value of the tar lost during that year by the use of beehive ovens amounted to approximately \$12,000,000. That the use of by-product ovens is increasing in greater proportion than the use of the beehive oven is shown by the fact that for the former type the increase in 1910 over 1909 in tons of coke produced was 14.13 per cent, while the production from beehive ovens increased by only 4.57 per cent. Parker adds, however:

While noteworthy progress has been made in the substitution of modern retort-oven practice for the wasteful and what should be obsolete beehive or partial-combustion method of coke making in the United States, this country is still much behind European countries in this regard.

He says further:

The yield of coal in coke in retort ovens exceeds that obtained in beehive or other partial-combustion ovens by about 15 per cent, and generally the quality of the coke is improved.

In order to determine the character of coke oven tars at present being produced in the United States, it was first necessary to obtain samples from all of the known plants, and for this purpose reference was made to a list of by-product and retort coke oven plants of the United States and Canada (Jan. 1, 1910), which was kindly loaned to Mr. Hubbard by Mr. Parker in advance of its publication.² Letters were then written to each plant asking for the following information:

- (1) a. At what maximum temperature are your retorts fired in your ovens? In your ovens?
- b. What is the maximum temperature to which the charge of coal is brought in your ovens? In your ovens?
- (2) What is the specific gravity of your crude tar in your ovens? In your ovens?
- (3) What percentage of free carbon is found in your crude tar from your ovens? From your ovens?
- (4) Will you furnish us for examination a 1-gallon sample of your crude tar from your ovens? From your ovens? To be sent at our expense.

Very courteous replies were received from the manufacturers, and in practically every case samples of tar

¹The Manufacture of Coke in 1910. United States Geological Survey.

were also forwarded. The blanks in these questions were filled out by inserting the names of the type or types of ovens operated by the manufacturer to whom they were sent. It was found that where two types of ovens were operated at the same plant, no attempt was made to separate the tar, and the entire output was run into a common well. In such cases the sample of tar submitted was a mixture obtained from both ovens.

The questions concerning temperature were asked because criticism from an authoritative source had been received with regard to a statement made by the author in a former publication³ to the effect that in the production of tar from by-product coke ovens "*carbonization is conducted at a lower temperature than in the manufacture of coal gas*." The resulting tar therefore contains a smaller amount of free carbon, averaging from 3 to 10 per cent. * * * But little reliable information on this subject could be obtained from published literature, although the opinion seemed to prevail that carbonization in by-product coke ovens is conducted at a lower temperature than in modern gas house practice. Thus, according to Lunge,⁴ "Hilgenstock (J. Gasbeleucht, 1902, 617) attributes the notorious difference between gas tar and coke oven tar with respect to their contents of free carbon and other products of pyrogenetic decomposition to the fact that in coke ovens the escaping vapors do not attain temperatures above 600° C., and that they are moreover protected against decomposition by the dilution of the heavy vapors, slowly given off from the interior of the coal block, with the fire-resisting gases escaping at the same time from the outer zone of the block. On the other hand, in the case of gas retorts, the heavy vapors escape at once undiluted by the fire-resisting gases which are set free afterwards, and the heavy gases are thus exposed to the white heat of the upper part of the retort."

Answers given by the manufacturers with respect to this question indicate only an approximate knowledge. In general it may be said that carbonization below 970° C. is considered low temperature, from 970° C. to 1,100° C. medium temperature, and from 1,100° C. to 1,540° C. high temperature; and that modern gas house practice involves the use of high temperatures. However this may be, it is not the purpose of this circular to compare coke oven tars with gas house tars, but to consider the former with relation to their utility as road materials.

From a total of 31 manufacturers to whom the questions were submitted 30 replies were received, but 4 of these reported their plants as not in operation. The remaining 26 furnished samples of their crude tar for examination and answered the questions in so far as they were able. Upon receipt of each sample the en-

tire contents of the package were thoroughly mixed and a representative sample taken from analysis.

The statements relative to the maximum temperature to which the coal is brought during distillation indicate that two of the plants run below 970° C., that a total of 22 run not over 1,150° C., that 9 run from 950° C. to 1,150° C., and that only 5 run above 1,150° C. The maximum temperature of firing the retorts is, however, reported in most cases as being higher than the maximum temperature to which the coal is brought.

The maximum percentage of free carbon reported is from 16 to 24 per cent, but 17 manufacturers reported the maximum percentage of free carbon as being 12 per cent or under, and only 4 as 16 per cent or over.

Analyses of the samples received were made in accordance with the methods described in a former publication⁵ of the office. The work consisted in determining the specific gravity, free carbon, or organic matter insoluble in c. p. carbon disulphide upon a 15-minute digestion at room temperature, material soluble in carbon disulphide, percentage of ash, and percentage of different fractions obtained by distilling a 250 c. c. sample in a 750 c. c. tubulated glass retort with the thermometer so placed that the top of the bulb was level with the bottom of the juncture of the stem and body of the retort.

The gravities of the samples examined range from 1.133 to 1.214 and the great majority were lower than 1.200. This in itself indicates low percentages of free carbon. The minimum percentage of free carbon was 2.73, the maximum 16.80, and the average for the 26 samples 8.38. Eighteen samples contained less than 10 per cent of free carbon and 8 more than 10 per cent. About two-thirds of these products might therefore be considered as low carbon tars and the other third as medium carbon tars. The amount of ash in no case exceeded 0.16 per cent, and in most cases it was practically nil. This is, of course, also true of practically all gas house coal tars. The percentage of water present varied from a trace to 10.1 per cent by volume, but in only 3 instances did it exceed 5 per cent. Water is a variable, depending upon a number of conditions, and as it is not a part of the true tar, has been eliminated in Table I. It is of interest to note that 14 of the pitch residues remaining after distillation had been carried to 315° C. were either soft or plastic—a condition which has seldom been noticed by the author in the distillation of gas house coal tars. The amount of solids which crystallized or precipitated out of the different fractions was found to vary greatly.

The results given in Table I are calculated upon a water-free basis; i. e., the percentages are expressed in terms of the actual tar exclusive of water. Considering these products according to type, it will be seen that the tar produced by the Koppers ovens contains the lowest percentage of free carbon, the Semet-Solvay tars the next lowest, the United Otto next, the Otto Hoffman next, and the mixed tar from the United

²Mineral Resources of the United States, 1909, Part II, pp. 240-242, United States Geological Survey.

³Circular 93, Office of Public Roads, U. S. Department of Agriculture, p. 9.

⁴Coal Tar and Ammonia, 4th ed., part I, p. 23, Van Nostrand.
⁵Bulletin 38, Office of Public Roads, U. S. Department of Agriculture.

ANALYSIS OF CRUDE COKE OVER TARS PRODUCED IN THE UNITED STATES AND CANADA

General Information			Answers to questions					Examination, Office of Public Roads										Serial No.			
Company and location.	Type of oven.	Maximum temperature of firing retorts.	Maximum temperature to which coal is brought.	Specific gravity of crude tar.	Per cent of free carbon in tar.	Spec. eff. of gray if tar, 25° C.	Per cent of free carbon.	Per cent of ash in H ₂ O.	Per cent soluble in (CS ₂) incl. H ₂ O.	Distillation result.								Pitch			
										Water	Light oils up to 110° C.	Middle oils, 110°-170° C.	Heavy oils, 170°-270° C.	Heavy oils, 270-315° C.	Per cent by weight.	Per cent by volume.	Per cent by weight.		Per cent by volume.	Per cent by weight.	Per cent by volume.
5126 Solway Process Co., Syracuse, N. Y.	Sealed Solway	1050-1450° C.	950-1150° C.	1.12-1.21	3-12	1.195	7.76	0.12	92.12	1.0	0.8	0.3	0.8	11.5	19.8	7.3	576.6	79.1			
5123 Senet Solway Co., Pennsylvania Steel Co., Steelton, Pa.	do	1050-1450° C.	950-1150° C.	1.12-1.21	3-12	1.206	8.77	0.07	91.16	1.0	8	4	3	12.3	20.9	6.9	267.4	77.6			
5124 Senet Solway Co., National Tube Co., Benwood, W. Va.	do	1050-1450° C.	950-1150° C.	1.12-1.21	3-12	1.176	7.14	0.04	92.82	1.1	1.0	1.9	1.5	13.2	21.9	10.6	369.5	73.3			
5137 Senet Solway Co., Milwaukee Coke & Gas Co., Milwaukee, Wis.	do	1050-1450° C.	950-1150° C.	1.12-1.21	3-12	1.168	6.10	0.05	93.85	1.8	1.5	1.4	1.2	18.9	15.5	4.9	368.4	72.5			
5121 Senet Solway Co., Pennsylvania Steel Co., Lehigh, Pa.	do	1050-1450° C.	950-1150° C.	1.12-1.21	3-12	1.173	4.71	0.06	95.23	6	5	1.6	1.3	15.3	19.4	8.4	70.1	73.7			
5125 Be Products Coke Corporation, South Chicago, Ill.	do	1050-1450° C.	950-1150° C.	1.12-1.21	3-12	1.191	7.49	0.03	92.48	(?)	4	3	1.1	9	23.6	20.7	3.9	65.1	68.9		
5128 Senet Solway Co., Detroit, Mich.	do	1050-1450° C.	950-1150° C.	1.12-1.21	3-12	1.169	6.56	1.1	93.33	6.9	5.9	2.3	4	13.0	16.9	5.7	368.4	72.0			
5200 Senet Solway Co., Empire Coke Co., Geneva, N. Y.	do	1050-1450° C.	950-1150° C.	1.12-1.21	3-12	1.159	6.07	0.08	93.85	4.0	3.4	2.6	2.1	15.5	11.4	10.4	563.8	67.7			
5189 Senet Solway Co., Dunbar Furnace Co., Dunbar, Pa.	do	1050-1450° C.	950-1150° C.	1.12-1.21	3-12	1.181	8.85	0.02	91.13	2.0	1.7	1.4	2	17.8	16.5	5.7	269.6	73.1			
5160 Senet Solway Co., Central Iron & Coal Co., Tuscatossa, Ala.	do	1250° C.	1150° C.	1.17	5.72	1.159	5.05	0.02	94.93	3.2	2.8	2.4	1.9	16.3	17.5	6.8	568.0	71.5			
5074 Philadelphia Suburban Gas & Electric Co., Chester, Pa.	do	1050° C.	1000° C.	1.16 (20° C.)		1.141	3.96	0.05	95.99	2.3	2.0	2.3	1.3	12	18	22.8	19.5	57.8	62.6		
5081 Senet Solway Co., Ensky, Ala.	do	1250° C.	1150° C.	1.17	8	1.175	6.90	0.06	93.04	3.3	2.8	1.4	1.0	2	16.5	14.1	19.3	8.2	569.3	73.2	
5095 The New England Gas & Coke Co., Everett, Mass.	Otto Hoffmann.	1100° C.	1200° C.	1.17	8-10	1.160	13.94	0.00	86.06	2.2	2.0	2.9	2.3	6	5	23.5	20.4	15.6	14.4	555.2	59.7
5083 Lackawanna Steel Co., Lackawanna Iron & Steel Co., Lehigh, Pa.	do	1000° C.	1000° C.	1.10	16-24	1.214	14.05	1.3	85.82	5.4	4.4	9.1	1.4	9.1	11.3	11.9	19.4	8.1	707.7	74.6	
5159 Dominion Tar & Chemical Co., Sydney, Nova Scotia.	do	1800° F. (?)	1800° F. (?)	1.170	10-15	1.143	10.81	0.05	89.14	3.2	2.8	1.9	1.5	6	5	27.2	24.2	19.7	6.7	559.8	63.5
5107 Hamilton Otto Coke Co., Hamilton, Ohio.	do	1111° C.	1111° C.	1.14	6-10	1.160	8.37	0.06	91.57	3.4	3.0	3.1	2.5	7	6	27.9	24.1	13.8	3.5	561.1	64.9
5086 Carnegie Steel Co., South Sharon, Pa.	United Otto	1665° F.	1444° F.	1.2	7.09-10.64	1.191	7.89	0.03	92.08	1.0	1.0	9.6	1.2	6	4	162.1	10.2	11.0	9.7	373.7	77.5
5078 Maryland Steel Co., Sparrows Point, Md.	do	1335° F.	1222° C.	1.119	8-10	1.179	8.49	0.03	91.48	1.6	1.3	1.3	9	6	4	117.2	15.1	19.6	8.5	269.7	73.2
5087 Citizens Gas Co., Indianapolis, Ind.	do	1222° C.	1222° C.	1.114-1.15 (50° F.)	4-5	1.133	5.21	0.07	94.72	1.2	1.1	1.1	9	14	13	23.9	21.4	11.6	10.4	560.8	64.7
5109 Pittsburgh Gas & Coke Co., The United Coke & Gas Co., Glassport, Pa.	do	(?)	(?)	1.207 (16° C.)	16-59	1.176	10.53	0.04	89.43	1.1	1.0	1.1	9	5	4	182.9	23.6	11.6	6.3	563.5	67.6
5122 Zenith Furnace Co., Duluth, Minn.	do	1222-1277° C.	2200-2300° F.	(?)	(?)	1.195	12.18	0.05	87.77	3.6	3.0	1.7	1.3	4	3	118.1	15.9	12.5	11.1	563.7	67.8
5188 Illinois Steel Co., Joliet, Ill.	Koppers	1444° C.	1388° C.	1.16-1.20	12-15	1.171	3.89	0.06	96.05	1.9	1.6	9.7	1.2	2	2	20.0	18.0	13.4	12.0	362.8	66.3
5404 Illinois Steel Co., Indiana Steel Co., Gary, Ind.	do	1100° C.	880-950° C.	1.174 (1.169)	4-35	1.169	2.73	0.04	97.23	3.5	3.0	9.3	1.0	4	3	120.6	18.5	9.7	6.5	267.1	70.2
5108 Canadian Coke Co., Camden, N. J.	Otto Hoffmann.	1000° C.	833° C.	1.20-1.30 (7.3)	7-9	1.182	11.30	0.06	88.64	2.2	1.9	1.8	1.4	6	5	120.5	18.2	18.5	7.5	266.4	70.1
5127 Cambria Steel Co., Johnstown, Pa.	United Otto.	1111° C.	1111° C.	1.12	15	1.211	12.40	0.16	87.44	10.1	8.3	9.3	2.3	9	3	9.7	6.1	12.7	6.9	372.0	74.8
5089 Lackawanna Steel Co., Buffalo, N. Y.	United Otto.	1000° C.	1000° C.	1.16	16-24	1.210	16.80	0.00	83.20	2.7	2.2	10.5	3	92.2	1.7	11.7	9.9	11.8	10.2	371.1	75.0

¹ Approximately.
² No information.
³ Varies with coal, coal with 28 per cent of volatile matter used.
⁴ With H₂O.
⁵ At present.
⁶ Variable.
⁷ Trace of solids.
⁸ Distillate, solid.
⁹ Distillate, one-fourth solid.
¹⁰ Distillate, nine-tenths solid.
¹¹ Distillate, three-fourths solid.
¹² Distillate, eight-ninths solid.
¹³ Distillate, one-half solid.
¹⁴ Distillate, two-thirds solid.
¹⁵ Distillate, four-fifths solid.
¹⁶ Distillate, seven eighths solid.
¹⁷ Distillate, one sixth solid.
¹⁸ Distillate, one fifth solid.
¹⁹ Pitch, soft and sticky.
²⁰ Pitch, very soft and sticky.
²¹ Pitch, hard and brittle.
²² Pitch, plastic.

Otto and Rothberg ovens contains the highest percentage of free carbon. For the sake of comparison the minimum, maximum, and average percentages of free carbon for each of these types are shown in Table II.

TABLE I.—ANALYSIS OF COKE-OVEN TARS UPON A WATER-FREE BASIS.

Serial number.	Type of oven.	Percentage of free carbon.	—Fractions by weight—				
			Percentage up to 110° C.	Percentage from 110-170° C.	Percentage from 170-270° C.	Percentage from 270-315° C.	Percentage of pitch.
5126	Semet-Solvay ...	7.82	0.30	0.70	11.59	7.35	79.73
5123	...do.....	8.84	.30	1.71	12.39	6.95	78.22
5121	...do.....	7.21	1.55	.60	13.33	10.70	73.83
5137	...do.....	6.19	1.21	.60	19.18	4.97	73.60
5121	...do.....	4.73	1.30	.60	15.57	8.44	74.07
5125	...do.....	7.49	.30	.90	20.70	8.90	68.90
5128	...do.....	6.97	2.44	.31	13.81	6.05	76.51
5200	...do.....	6.28	2.17	.51	16.04	10.76	70.08
5189	...do.....	9.00	1.42	.20	18.10	5.79	74.36
5160	...do.....	5.19	1.95	.30	16.76	6.99	73.55
5074	...do.....	4.04	1.32	.81	19.89	12.75	63.87
5081	...do.....	7.09	1.02	.20	14.50	8.43	75.30
5095	Otto Hoffman....	14.22	2.34	.51	20.81	14.69	60.91
5083	...do.....	14.69	1.46	.10	11.40	8.47	78.03
5159	...do.....	11.12	1.54	.51	24.89	6.89	65.32
5107	...do.....	8.62	2.57	.61	25.15	3.60	66.90
5086	United Otto.....	7.96	1.21	.40	10.30	9.79	78.28
5078	...do.....	8.60	.91	.40	15.29	8.61	74.16
5087	...do.....	5.26	.91	1.31	21.63	10.51	65.41
5109	...do.....	10.63	.90	.40	23.83	6.36	68.28
5122	...do.....	12.55	1.34	.30	16.39	11.44	69.80
5188	Koppers	3.95	1.21	.20	18.29	12.19	67.37
5404	...do.....	2.81	1.03	.30	19.07	6.70	72.37
5108	Otto Hoffman and United Otto....	11.51	1.42	.50	18.55	7.64	71.45
5127	...do.....	13.52	2.50	.21	6.65	7.52	81.57
5089	United Otto and Rothberg	17.17	.30	1.73	10.12	10.42	76.68

The percentages of various fractions for the different types of tars overlap to such an extent that no detailed comparison will be made. The maximum, minimum, and average total distillates to 315° C. for the different types are, however, given in Table III.

TABLE II.—PERCENTAGE OF FREE CARBON IN COKE-OVEN TARS.

Type of oven.	—Percentage of free carbon—		
	Minimum.	Maximum.	Average.
Koppers	2.81	3.95	3.38
Semet-Solvay	4.04	9.00	6.74
United Otto	5.26	12.55	9.00
Otto Hoffman.....	8.62	14.69	12.16
Otto Hoffman and United Otto (mixed)	11.51	13.52	12.51
United Otto and Rothberg (mixed)	17.17	17.17	17.17

From this table it is evident that wide variations exist in the relation of total distillate to pitch residue in the coke oven tars produced in this country, and this is even true of different tars produced by the same type of oven.

Straight coal tar road binders or refined coal tars are usually manufactured by subjecting the crude material to a process of distillation with or without steam or air agitation. Distillation is carried to the point at which the residuum remaining in the still has obtained the desired consistency at normal temperatures, and this involves the removal of certain of the more vola-

tile oils present in the crude material. For use in construction work a soft and almost fluid pitch is often produced, and the consistency of this pitch is controlled by means of a melting point or float test. When the crude tar runs abnormally high in free carbon it is sometimes mixed with crude water gas tar before distillation. Water gas tar contains a very low percentage of free carbon, and by properly proportioning the two a product is obtained upon distillation which does not carry more than the maximum limit of free carbon set by manufacturers. What the maximum limit should be is a much mooted question among those who have given thought to this matter. The governing considerations are: (1) What is the most economical limit from the standpoint of manufacture, and (2) what is the proper limit with regard to the utilization of the product as a road material? For a number of reasons, which it is unnecessary to mention in this circular, an excessively high carbon tar is difficult to distill properly, and, with other things equal, the lower the percentage of carbon the easier and shorter the distilling process. From this standpoint therefore by-product coke oven tars are well adapted to the manufacture of road binders. Moreover because of their low percentage of free carbon they may be employed in a manner similar to water gas tars, when it is desired to utilize a crude high carbon tar in the production of a medium carbon tar road binder.

TABLE III.—PERCENTAGE BY VOLUME OF TOTAL DISTILLATE TO 315° C. IN COKE-OVEN TARS.
[Water-free basis.]

Type of oven.	—Percentage by volume—		
	Minimum.	Maximum.	Average.
Koppers	30.5	36.0	33.3
Semet-Solvay	22.6	40.8	29.9
United Otto.....	25.6	38.5	32.6
Otto Hoffman.....	25.3	43.6	36.0
Otto Hoffman and United Otto (mixed)	19.9	32.1	26.0
United Otto and Rothberg (mixed)	26.9	26.9	26.9

In an ordinary road tar for use in construction work where free carbon is present to the extent of about 20 per cent, the proportion of total distillate, below 315° C., to pitch residue is approximately 1 to 4. Where this relation exists the pitch residue is hard and brittle. A residue which is soft or plastic is to be preferred, as it would indicate longer life during service; and where such a residue is present the proportion of distillate would naturally be lower for a given consistency, as the distillates may be considered as fluxes for the residues. If such is the case it is evident from the foregoing tables that coke oven tars offer a valuable source of supply for tar road binders. As an example, even the highest carbon tar analyzed, if distilled to the point where the proportion of distillate, below 315° C., to the pitch residue was as 1 to 4, would contain less than 19 per cent of free carbon, which is at present considered as not excessive for a refined coal tar.

In conclusion it may be said that indications point strongly to the fact that by-product coke oven tars will eventually play a most important part in the road ma-

terial industry, and it is to be hoped that their general adoption in this country will be rapid. The future demand for economical bituminous road binders in the United States will undoubtedly exceed the supply, and this in spite of the natural increase in petroleum and asphalt road binders. If such is the case, the present loss of enormous quantities of tar, to say nothing of gas and ammonia, because of the use of beehive ovens, is a matter worthy of the utmost consideration on the part of all who are interested in the conservation of our resources.

TUNGSTEN IN GERMANY.

The U. S. Consul at Hamburg, Germany, reports that Germany offers the largest market for tungsten, or wolfram, ore in the world, although the domestic uses of the metal are exceedingly limited as contrasted with its uses in England and the United States, which together absorb probably two-fifths of the total production. The metal itself is employed chiefly for hardening steel, and its varied applications are increasing rapidly. Hamburg importers are in a position to sell offerings of ore practically in unlimited quantities. The price is based on the content of tungstic acid (WO_3) the usual content running from 60 to 65 per cent. Ores under 60 per cent are not in demand. The ordinary commercial terms are Hamburg weight, analysis by the State laboratory, shipments in bags of 50 kilos (kilo = 2.2046 pounds), price per ton of mineral and per cent of tungstic acid. One thousand tons of 60 per cent ore should produce about 400 kilos of metal worth at the present time (January, 1912) 5.75 marks (\$1.37) per kilo, containing 97 per cent of metal, 0.1 per cent of carbon, and free from impurities. The total importations of tungsten ore into Germany in 1910 amounted to 2,491 tons, against 2,520 tons in 1909. The exports of the metal are included with exports of chrome and cadmium, the total shipments under the three heads being 1,643 tons in 1910 and 1,213 tons in 1909. American manufacturers imported ore and its products from Hamburg alone, as follows:

	1910.	1911.
Tungsten ore	\$143,620	\$53,410
Tungsten metal	126,967	
Tungsten filament lamps, ...		14,938

The metal is obtained by reducing the oxides or chlorides in a current of hydrogen, or by means of carbon in an electric oven. According to German patent No. 141811, the raw material is melted at a temperature of 300° with sodium bisulphate, after which the temperature is raised to about 800°, and lime or lime salts and alkalis of chlorine are added. Sodium bisulphate must always be contained in the mixture in excess of the other material. If the method is thoroughly carried out, all wolfram is obtained in the form of wolframic acid, or natrium wolframate (sodium tungstate). The wolframic acid is melted and thus reduced to metallic wolfram.

POTASH FROM THE PACIFIC KELPS.*

During the spring and early summer of 1911, systematic work was inaugurated to determine the fertilizer resources of the United States. Sources of supply for phosphoric and nitrogenous fertilizers were more or less well known. There was no known source of potash salts, however, of any economic importance. It is obviously desirable that such a source should be found and developed, and this fact was accentuated by the controversies arising between the "Kali Syndicate" and certain American importers which received much notice in the current press and was the occasion of animated diplomatic exchanges between the governments of the parties to the controversy. The resources of the United States in possible sources of "potash" therefore received special attention, and various lines of inquiry were actively prosecuted. One of these, so far, has yielded positive results. Balch (Jr. Ind. & Eng. Chem., 1-777) has called attention to the giant kelps of the California coast as occurring in enormous quantities and being especially rich in potash salt. Samples of the kelp from Southern California and the salts derived therefrom were submitted to this office by Mr. Balch in September, 1910, and further data were secured from various sources.

In the work this summer something over one hundred square miles of kelp groves were surveyed, and there is reason to believe that the total area on the Pacific Coast, from Magdalena Bay to Shumagin Islands, may possibly be 6 or 8 times this. Quite a large number of kelp and rockweeds were found, although generally the larger groves are approximately "pure stands." Two of the kelps are chiefly of importance as sources of potash. In the northern groves the important kelp is the *Nereocystis luetkeana* and in the southern groves it is the *Macrocystis pyrifera*. From Point Sur southward this latter occurs in large groves sometimes several square miles in area, and often in very dense masses.

Nereocystis grows in almost any depth of water, where there is a rocky bottom and also a strong tide-way or otherwise continual movement of the water. *Macrocystis* grows only on exposed coasts where there is much movement of water, and practically always at depths of from 6-10 fathoms. As the carbon dioxide and the oxygen necessary to the metabolism of the plant must be obtained from the dissolved gases in the water a continually renewed mass of water must be available. This fact, probably, accounts for the difficulties encountered in trying to artificially propagate these algae under laboratory or aquaria conditions. A rocky bottom is essential for the holdfasts which these plants have in lieu of roots, and to anchor them.

Nereocystis is an annual. The fruiting season is about over by the middle of July, and in order to maintain the groves this algae should not be cut before that time. *Macrocystis*, however, is probably a perennial;

*From the Journal of Industrial and Engineering Chemistry.

at least, its life is more than a calendar year, and if cut early in the summer, it is said to be able to regain its luxuriant growth in 40 days or thereabout. At least two cuttings, therefore, should be practicable. Its habit of growth, moreover, the spores forming on fronds well below the surface, tends to provide against its extinction or serious depletion. Nevertheless, it would probably be wise to maintain a "closed season" for this algae also and not permit more than two cuttings per season, thus insuring a sufficient fruiting to maintain the groves unimpaired. Some form of governmental protection or control of the groves is obviously necessary to their maintenance and efficiency.

The cutting and harvesting of the kelp is a detail of the industry which is in a far from satisfactory shape. Several forms of cutters have been suggested and a few tried. This is, however, a mechanical detail which American ingenuity will unquestionably settle soon now that it has been shown to be worth while. It probably will not be practicable to cut the kelp more than 10 or 12 feet below the surface of the water, and in the case of the *Macrocystis* at least a greater depth of cutting should not be permitted, in order to insure fruiting and reseedling of the groves.

Kelp was originally a term applied to the ashes of seaweeds and rockweed, but has become, especially in this country, synonymous with the seaweeds or brown floating algae, and on the Pacific Coast is applied popularly to the two plants cited above. These plants among other characteristics have this in common, they absorb relatively large amounts of potassium chloride from the sea water, much larger than most other algae either of the Pacific or other waters. Dr. J. W. Turrentine has made a large number of analyses. From his data it appears that *Nereocystis* contains about 30 per cent of its dry weight potassium chloride and *Macrocystis* nearly as much. With both kelps, as they dry out, large quantities of potassium chloride, mixed with varying amounts of other salts, effloresce on the surface, and can be removed readily by simply shaking. Practically all the potassium salts can be obtained by lixiviation of the dried plant or of its ash.

Neither *Nereocystis* nor *Macrocystis* of the Pacific littoral contain as much iodine as many other seaweeds and rockweeds. Nevertheless, the amounts present are notable and contrary to popular belief; the southern kelp contains more than does the northern.

According to Turrentine's analyses *Nereocystis* contains about 0.16 per cent and *Macrocystis* about twice as much. Besides iodine, other useful products can be obtained from these kelp, of which, however, space will not permit a discussion here.

It is not possible as yet to give an accurate estimate of the amount of potassium chloride which the Pacific kelp groves can yield annually. With all conditions at their best the maximum possible yield might be in the neighborhood of 8 million tons, worth at present prices about \$300,000,000. No such yield is probable, however, at least in the near future. Taking every con-

sideration, and leaning strongly to conservatism it may be said that it ought to be perfectly practicable to obtain an annual yield of at least a million tons of potassium chloride, worth at present prices upwards of \$30,000,000. The iodine obtainable at the same time should go far toward paying the expenses of harvesting the kelp and extracting the potash.

It has been assumed in some quarters that because the kelp can be made to yield about three times the present total potash importations from Germany the latter will be stopped or greatly diminished. This is very much to be doubted. Existing business engagements will ensure continued importation for some years to come. It is possible, and greatly to be desired, that potash from American kelp will reduce the price of potash salts. But the vast bulk of the potash salts goes into the South Atlantic states because these states at present are the great fertilizer consumers. Inevitably the Trans-Mississippi states must soon use fertilizers and in fact the movement has already begun. A very large increase in the consumption of fertilizers, and therefore of potash, may be anticipated within the next few years, enough probably to take up the American production in sight and the importation to be obtained from Germany as well.

The great importance of the kelps lies not in the probability of their excluding German potash, but (1) if properly managed, in preventing a monopoly and regulating prices; (2) in making possible a greatly extended use of fertilizers, and thereby perhaps even stimulating importations; and (3) in times of stress, giving the country a resource and preventing the agricultural interests from being at the mercy of an outside power.

The U. S. Consul at Hull, England, reports that experiments are now being made at some of the crushing mills in Hull as to the feasibility of extracting oil from sunflower seed and using the residue as an ingredient in the manufacture of feed cake. Large consignments of seed have recently arrived in Hull from Odessa, the sunflower being extensively cultivated in southern Russia. When crushed the sunflower seed yields on the average 30 per cent of oil, while the yield of soya-bean oil is 18 per cent. The oil is limpid and pale yellow in color, and it is believed it will prove valuable in soap making, the manufacture of varnishes, and for culinary purposes. The residue from the crushed sunflower seeds has been manufactured into cakes, and experiments are being made to ascertain whether the cake thus made is suitable for feeding purposes. A small quantity of these cakes has been shipped to the Continent. Experiments have not gone far enough to give any exact data as to the value of the oil or the meal. No market prices can be stated as there has been no demand, and no trustworthy comparison with other oil and cake producing seeds can be given as yet.

UTILIZING WASTE WOOD BY DESTRUCTIVE DISTILLATION.*

By JAMES LAWRENCE and JAMES C. LAWRENCE.

Although the wood that is annually wasted by the logging and lumber industries of the United States is commonly thought to be a great amount, it is doubtful if the real figures are familiar to every one. According to the statistics of the U. S. Forest Service and based on a figure of 65.16 per cent waste given by Frankforter,¹ there were in 1907 150,000,000 tons of wood wasted. By intensive utilization the greater part of this could have been saved. We will take up only one phase of the question, however, that of utilization by destructive distillation, and will limit ourselves further by dealing only with those products obtainable from hardwoods, principally oak.

The immediate products obtained by destructively distilling oak are well known—viz.: pyroligneous acid liquor containing acetic acid and methyl alcohol, tars and oils, charcoal, and uncondensed gases. Some of these yield other substances of commercial importance on further treatment. The acid liquor may be neutralized by milk of lime after freeing from tarry matter, and the alcohol or crude wood spirit then distilled off. At present there are processes of carrying out this procedure in one continuous operation.² The wood spirit may then be rectified further if deemed necessary, although there is one apparatus manufacturer at least who claims to be able to produce 99 per cent methyl alcohol in one step. The tars can also be redistilled and the more valuable creosote oils obtained. The gas is (or may be) used for heating the retorts or ovens during a part of the distillation. The charcoal after cooling is ready for market without further treatment.

Until recently it was thought that wood less than 4 to 6 ins. in diameter could not be advantageously used for destructive distillation because of the tendency toward burning away too rapidly when the exothermic reaction commenced. This reaction starts at about 275° C.³ and if external heat is applied causes the formation of decomposition products from the acetic acid and methyl alcohol. This burning up is especially true of sawdust, which fact is readily understood when the finely divided condition and large exposed surface is considered. However, a patent has recently been granted in England⁴ for a retort which uses sawdust. It is essentially an endless screw which feeds the sawdust over the heated portion of the retort slowly and a little at a time. We are unable to state what results have been obtained in practice with this apparatus, but a moment's consideration

will reveal the great saving to lumbermen if it is practicable.

If the destructive distillation industry is to use only 5 or 6 in. cordwood there will be very little chance of utilizing any lumber waste, hence it occurred to the authors that some data might be obtained on the effects of using only mill waste for this purpose, and some statistics compiled from actual observation are appended.

The experimental data were obtained from oak lumber slabs and "offal," the slabs measuring 1 in. to 2 ins. thick, 2 ins. to 4 ins. wide, and were cut into lengths of 2 ft. The charges were of 200 lbs. each, and both green and air dried woods were used. The green wood gave a greater yield of acid liquor, but the yield of acetate obtained from this was lower in proportion than that from dry wood. This was doubtless due to the moisture present causing decomposition of the acetic acid and methyl alcohol, and also to the increasing of the volume of the distillate by water.

Since it has been shown that such finely divided wood as sawdust may be destructively distilled with suitable apparatus by heating carefully a small quantity at a time, it was decided to attempt distillation on the same principle, using slabs. It is also known that when wood is distilled a reaction which generates heat sets in at about 275° C., and it was assumed that if the retort were allowed to cool at this point the internal heat would not increase to such an extent as to decompose the alcohol and acetic acid formed. Therefore, when the yield of distillate reached a maximum the external heat was withdrawn and the distillation was allowed to proceed alone. Theoretically the wood should char itself completely after this point is reached, but on allowing it to cool and then heating some of the charcoal in a glass retort afterwards it was found that a small percentage of distillate came off, and the charcoal was dark brown, and became black on heating. Our procedure was therefore modified so that the retort was heated very slowly up to 100° C., then a little more rapidly to 280°, and then the external heat was withdrawn until the temperature reached a maximum, when the heat was again applied, and the distillation finished as rapidly as possible, up to a little over 400°C. These operations gave the maximum amount of distillate obtainable, and the decomposition of the alcohol and acid was avoided as far as possible. The table will show the yields of products obtained from the distillations—the difference between the results from green and dry wood and the results of comparative rapidity of heating being noted.⁵ Appended to the table are given the products obtained in the distillation of the same species of wood (red oak) by Senff.⁶ He used only 5 lbs. of wood in his charges, and it was cut into very small sticks. He did not attempt to separate the alcohol from the pyroligneous liquor, and reported the yield of acid

*From the Journal of the Society of Chemical Industry. Some of the experimental data in this paper were presented at the December, 1910, meeting of the American Chemical Society

¹J. Ind. & Eng. Chem., 1911, 3, 6.

²Campbell, Met. & Chem. Eng., 1910, 8, 3

³Fawcett, J., Soc. Chem. Ind., 1885, 5. Klason et al. Angew. Chemie, 23, 1252.

⁴Halliday, Salford.

⁵Berichte, 1885, 18, 60.

⁶Figured to parts per 100 parts wood.

⁵Berichte, 1885, 18, 60.

⁶Figured to parts per 100 parts wood.

as acetic acid. In the table we have calculated this to acetate of lime for the sake of comparison.

As to statistics, we will take as an example of commercial utilization the wood wasted in a small lumber mill over a period of a few months, for which we have accurate figures from personal observation. The mill cut 125,000 ft. BM. of hardwood lumber. Using Frankforter's⁷ figures we find that there was wasted in stumps, slabs, limbs, etc., wood to the amount of 883,700 lbs., or 196.4 cords. Almost all of this could have been used for distillation. Taking the figures given as averages in the table of data, we find that this would have yielded products as follows:

Tar	Lbs.
Charcoal	30,488
Alcohol	274,919
Acetate of lime.....	9,544
	42,948

From statistics furnished by the U. S. Census Bu-

WASTE AND CONSERVATION OF POTASH AND PHOSPHORIC ACID.*

By F. K. CAMERON.

As far as the phosphates are concerned, there is a great deal of waste in the Florida fields. It varies there quite a little, but sometimes amounts to as much as 200 or 300 per cent; that is to say, for every ton of phosphate rock mined there and ground for fertilizer, twice as much phosphate rock in a comminuted condition generally is thrown away; wasted. In Tennessee, where large deposits of phosphate rock are found, the mining is very much cleaner than in Florida, and there is very little waste. The mining methods in that section have been greatly improved in recent years, and the waste is falling off. In the Charleston, S. C.,

TABLE OF YIELDS.

Parts per 100 parts of wood used.

No.	Parts of wood.	Condition of wood.	Acid liquor obtained.	Tars obtained.	Charcoal residue.	Crude Alcohol from acid liquor.	Acetate of lime from acid liquor.	Gas.	Remarks.
1	100	Green, bark on....	42.50	3.10	29.90	0.95	4.45	24.50	Heated slowly.
2	100	Green, bark off....	44.25	3.58	30.20	1.00	4.75	21.97	Heated slower than 1.
3	100	Green, bark off....	36.50	2.80	29.20	0.85	4.05	31.50	Heated rapidly.
4	100	Air dry, clean....	40.05	3.50	35.20	1.30	5.15	21.25	Heated slowly.
5	100	Air dry, clean....	44.50	3.70	31.60	1.20	5.05	20.20	Slightly dryer than No. 5. Heated slowly.
6	100	Air dry, clean....	40.65	5.75	31.25	1.20	5.15	24.35	Heated a little more rapidly than No. 6.
7	100	Air dry, clean....	42.75	3.55	30.00	1.15	5.00	23.70	Heated a little more rapidly than No. 6.
8	100	Air dry, clean....	44.25	3.63	31.56	0.95	4.95	20.56	Heated slowly.
9	100	Air dry, clean....	43.75	3.45	31.12	1.15	5.05	21.68	Heated slowly.
Averages				3.45	31.11	1.08	4.86		
1	100	Air dry, bark on..	44.45	3.70	34.68		4.55	17.17	Heated slowly.
2	100	Air dry, bark on..	42.04	3.20	27.73		3.84	27.03	Heated rapidly.

*No. 4 was run with sawdust and burned up on heating too rapidly.

reau for 1909 these would have the following values:

Tar at 8 cents per gal.....	\$ 250.00
Charcoal at 6 cents per bu.....	825.00
Alcohol at 24 cents per gal.....	1,865.00
Acetate at 1.5 cents per lb.....	644.00

Total

In a small commercial plant of about ten cords capacity per day this would have taken less than three weeks to work up. These small figures were taken, contrary to the usual custom of speaking in sums far above ordinary comprehension, to indicate approximately the great field of saving in natural resources which the chemist and chemical engineer can effect.

As a matter of interest we submit below an analysis of a sample of the gas taken from one of the distillations, and would call attention to the high calorific value of this gas for a "wood gas."

	Pct. vol.
Heavy Hydrocarbons	8.16
Marsh gas	12.32
Carbon monoxide	35.08
Carbon dioxide	31.45
Hydrogen	10.94
Nitrogen	2.05

100.00

Calorific value, 11,493 B. T. U. per lb.

fields there is still a great deal of waste.

The great problem in handling phosphates are to insist upon clean mining, and to develop methods for segregating phosphoric acid from the rock phosphate and thus make low-grade material available.

At the present time there is practically no high-grade rock, that is 72 per cent bone phosphate, used in this country. All of the high-grade rock that we mine, or practically all of it, is shipped abroad and the American market takes only the lower-grade material. It is improbable, so far as we can judge, that there will be any very great consumption of the high-grade material in this country so long as the foreign demand keeps up, and we have to utilize the lower-grade material.

The estimates which we have been able to make from the survey of the existing fields of this country, indicate that the deposits of the high-grade rock are so large that, at three times the present rate of consumption in this country, it would last something like 1200 years; that is, excluding any new discoveries. We have not only the Florida fields, the hard rock, the pebble rock, the Charleston field, the Arkansas field, the Kentucky field and the Tennessee field, but the

largest deposits of high-grade rock in the world have been discovered in Montana, Utah, Idaho and Wyoming. There are a good many fields in this country that carry some phosphorus in the rock, which makes it useful locally from the fertilizer point of view; for instance, up in the Shenandoah Valley some rocks run two or three per cent phosphoric acid, and some deposits are known in North Carolina, along the Piedmont Plateau, that run quite high in phosphoric acid.

The next big waste that we have to consider is the nitrogen waste. This is more or less intimately connected with carbon waste, already discussed. By the introduction of a by-product oven in this country, we are saving some of the nitrogen from the coal, as well as making gas. Both the ammonia and the gas are finding a market, but their values depend largely upon the location of the plant, and the overhead charges, which vary with the different installations. That it pays can be illustrated by the fact that one concern in a coal-mining district is taking the product from the mine, coking it, returning it to the mine owner, and paying him a royalty on it, and it is paying him very handsomely; so much so that they have made a contract for a good many years.

For press of time I can only interject here the fact that we are making in this country about one-third as much ammonium sulphate as we are importing, and what we are getting is about one-eighth as much as it is possible to make from the coal being coked at the present time.

The amount of nitrogen that is wasted in the form of fish refuse is enormous, especially on the Pacific Coast. I have seen enormous amounts of fish refuse thrown in the rivers, a perfect nuisance to the towns, washing up along the shores and banks of the rivers, and no attempt being made to utilize this most valuable material.

One of the big carbon wastes, which might have been spoken of this morning, and which contains potash, nitrogen and phosphorus, is the city wastes—the garbage and night soil. There is very little effort made to conserve these. Some doubt exists in this country as to their value as fertilizer, it being claimed by some that it is practically nil, and we are at a loss to know what the true values of those materials are. Night soil is utilized very largely in China and Japan, and some of the American gardeners in this country also use it, but there is a great objection here to its use on account of the danger from pathogenic germs. It has been found to be very good fertilizer in those countries, while in Europe and this country it has not been found to be so good. But here it has not been used under the same conditions. All of the material of this kind used in Japan and China is first worked over in appropriate pits or vessels, and “fermented” before it is applied to the field.

The biggest problem of all, for us, has been the possibility of using raw materials, waste materials if you

please, for the production of potash salts. With the prospect for 1200 years of phosphates before us, we need not be very much worried at present on that score, and with the prospect of getting all the nitrogen we want from by-products of one kind and another, or by utilizing atmospheric nitrogen, bacteria, etc., we need have no serious concern on this score.

We have, however, been in a quandary as to what to use for potash, and the public mind has been very much exercised on account of the well known difficulties between this country and the one country that contains the principal source of potash for the world's supply, namely, Germany.

Now this country takes about one-fifth of the potash salts mined in Germany, and about one-half of the amount that is exported from Germany; and we had no other source of supply until quite recently. There is a possibility of our getting potash from some of the arid basins, of getting a small amount from smelter fumes, from wood ashes, and from sawdust. There is made annually in the lumber mills of this country something like 5,850,000 tons of sawdust. This is equivalent to about 5,200 tons of potassium carbonate. But when you recognize that it is scattered around the country, there is no possibility of its being of much importance for general use.

Practically all the salt wells in this country carry a small amount of potash, and when the water in the wells is evaporated, the mother liquors would give a material which compares fairly well with the so-called manure salts. It is possibly one of the waste products which could be used, but at present it will hardly pay.

Another source of potash in which people have been interested is the silicate rocks carrying potassium. There have been quite a number of processes suggested, patented or secret as the case may be, for extracting potash from silicate rock. It is possible to do so, but it is very difficult to do economically, and practically none of these processes as yet have any commercial value. There are several of them that are being tried at the present time, and some may later prove extremely valuable.

There is a silicate rock process that has given promise of becoming commercially valuable. The extraction of potash is commercially possible so long as they can get a certain by-product which, I am sorry to say, I cannot yet mention in public. This process is perfectly possible as a source of potash to the extent of 40 to 60 tons a day, but if they try to go beyond that they are certain to lose money, because they cannot get the necessary raw products, aside from the potash mineral, at figures which will enable them to make a profit. This is one of those very curious processes that the larger you make it the less it pays.

There is one substance which has been a waste product, and which has been a nuisance in that part of the country in which it grows, and that has turned out to be a very good source of potash.

Along the Pacific Coast of the United States and

*From the Journal of Industrial and Engineering Chemistry.

Alaska, there are a number of seaweeds, or kelps. In fact, we have them along the New England coast. The seaweeds have been used along the New England coast for fertilizers, and also along the coasts of the British Isles, Norway, Denmark, Sweden, the Hebrides, and have been considered extremely valuable. Kelp rights were one of the important assets of the owners along the coasts of the countries named. But kelps have heretofore been used principally as a source of iodine, and when iodine was developed from the mother liquors of the Chile saltpeter, kelps went out of fashion and little has been thought of them until quite recently.

In examining the Pacific kelps we found that some people were interested in them as a source of iodine, and some from the standpoint of their being a nuisance. When our attention was directed to this waste matter, we were at the same time interested in potash. We organized three parties to investigate the extent of these kelp areas mapped out the kelp beds in half of Puget Sound, and found that about 210,000 tons of the principal kelp were produced there annually; there is a great deal along the California coast from the Golden Gate down to Point Sur, and from Point Sur south there are enormous beds of very large kelps, the main kelp there being quite different from that growing in the Puget Sound region. Some of these beds along the Southern California coast, extend from two to five miles in length and from a half to two miles in width, or even larger, and some of the large beds are extremely thick. We have mapped this past summer about one hundred square miles of kelp beds, the two principal areas being in the north, in Puget Sound, and in the south, from Point Sur southward. The plants grow in strong tideways, or where they are exposed to the full force of the open sea. All of the groves are within the three-mile limit.

We have found that the kelps in the Puget Sound area, when dried, contain as much as 30 per cent potassium chloride and two-tenths per cent iodine. In the South, they contain 20 to 30 per cent potassium chloride and rather more iodine than those in the north. The kelps in the Puget Sound region (probably the same as those in Alaska) are annuals, are in best condition for cutting and have finished fruiting the latter part of July. If these kelp beds are to be a source of profit, they should be protected and should not be cut until after the middle of July. In the South, the important kelps are probably perennial and if cut not more than two feet below the surface, become as thick as before in about forty days.

It is quite impossible to give an exact estimate of the amount of potassium chloride in sight from this source. The analyses would indicate that the amount of potassium chloride to be obtained from these kelp is pretty big, so we are standing by a very conservative estimate of 1,000,000 tons as the probable production of potassium chloride from the Pacific kelp beds, if the

beds are properly protected. This gives a source of potash at least three times as great as the total potash importations from Germany. If the larger estimates prove true, it means a possible production of potassium chloride about the same, or even a little larger than the total production in Germany.

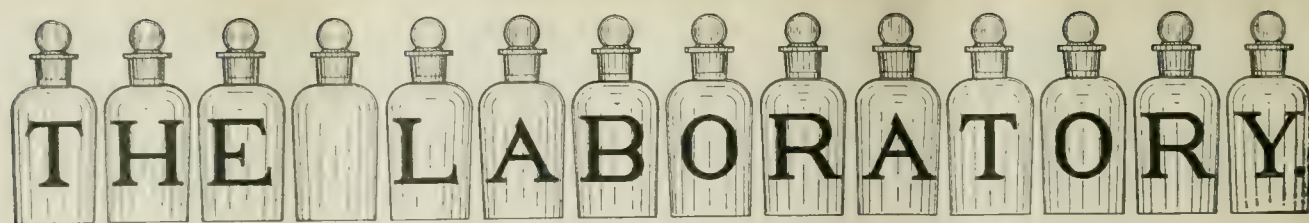
There are all sorts of things of interest in connection with these kelps as a present waste product. It is possible to make from them a number of foods which are used in Japan and elsewhere, known as Kombu. Another series of good products is known as Nori, and while it is probable we might develop an industry in the making of these things for the Japanese, it is rather improbable that the Americans will care for them.

It is, however, probable that a cattle food might be developed in this country from kelps. The nitrogen content of these kelps would place them about the same as hay, better perhaps than the ordinary eastern hay, if not as good as the best western alfalfa; and there is a possibility that the organic material could be used as roughage for cattle food after the salts had been extracted.

It is also estimated that the possible kelp production would give us an amount of iodine, which is easily recoverable apparently, worth about \$90,000,000, at present prices. These figures are possibly misleading, because the importations of iodine and iodine products, according to the figures of the Department of Commerce and Labor for the last year, would seem to be about \$1,000,000 worth annually.

To put the whole matter in a nutshell, if these beds are properly protected and no longer considered a waste product but a raw product of great value, if they are properly harvested, and if we attempt seriously to utilize the iodine and other products which can be made from them, we ought to be able easily to harvest a quantity which would yield annually at least 1,000,000 tons of potassium chloride, besides vast quantities of by-products, and thus make of what has hitherto been considered a waste and a nuisance, a source of enormous commercial value.

The manufacture of buttons from vegetable ivory is a highly developed branch of German industry. Germany imports a little over one-half of the total annual crop of vegetable ivory furnished by South America, and the bulk of the import is used in the manufacture of buttons. The industry is centered largely in the little town of Schmolln, in the Duchy of Saxe-Altenburg, where there are 14 factories and where, also, there are several important jobbing firms dealing exclusively in buttons. There is one factory at Breslau, and some manufacturing is done at Berlin and in the adjoining town of Charlottenburg.



MARKING PORCELAIN AND SILICA CRUCIBLES, ETC.

In the analytical laboratory there often is occasion to put permanent distinguishing marks upon crucibles, etc., which will stand ignition and mild treatment with acids and alkalis. The blue pencil or the brush and china paints which are frequently used for this purpose, the markings being burned in, often give results so crude as to be quite unsatisfactory, especially for articles that are before one's eyes daily for years. Moreover, the blue pencil marks and many china colors lack permanence, and when applied to silica wares do not adhere satisfactorily. Mr. P. A. Yoder, assistant chemist, Plant Physiological Laboratory, U. S. Bureau of Chemistry, has worked out two methods, one for marking with platinum and the other for the application of china paints, both by the use of rubber type. A description of these methods is given in a recently issued circular of the U. S. Bureau of Chemistry.

THE PLATINUM PROCESS.

The crucibles are cleaned by heating for half an hour with nitric acid, one part concentrated acid to one part of water. A sizing is prepared consisting of a hot 5 per cent solution of gelatine. The parts of the crucibles to be marked are dipped into this sizing and set aside to drain and dry. When the gelatine is dry, the desired number is stamped on with a solution of platinic chloride containing 12 to 15 per cent of platinum; i. e., about 32 to 40 per cent of the hydrated crystallized chloroplatinic acid. The pad holding the solution may be made of six or eight folds of smooth linen or muslin and need not be much larger than the type used. This pad is nearly saturated with a few drops of the platinic chloride solution. Too much of the solution causes blurring and too little of it or too diluted a solution results in dim numbers. After the numbers are dry the crucibles are gently heated until the platinum is reduced and the gelatine burned off. This is most conveniently accomplished in a muffle. Finally, the numbers are heated for one-half minute in the flame of the blast lamp—i. e., for one-half minute from the time it attains the temperature of the flame.

If the wares are cleaned and fired as directed, the markings adhere well. The figures become more prominent if burnished by use of a china painter's burnishing stone, if available, or of seashore sand, or less advantageously of a silica soap. The deposit is resistant to single acids, but not to alkalis. In some experiments library paste was substituted with good results for the gelatine sizing. Gold and mixtures of gold and platinum solutions may be applied similarly,

but there is more danger of volatilizing the gold chloride before reduction takes place, and thereby causing a spreading of the deposit. The resulting figures also are less conspicuous than when platinum is used. This method of getting the deposit of platinum or gold may possibly find use also in decorating chinaware. If the solution is applied with a brush, a quill, or a glass stylus, it may be more dilute. The same method applied to silica wares also gives very satisfactory results.

APPLICATION OF CHINA COLORS BY USE OF RUBBER STAMPS.

Paints mixed in oil are not satisfactory for use with rubber stamps because the type leaves on the porcelain a rim of thickened paint while the main surface of contact is relatively bare. The method finally adopted is to stamp the wares to be marked with a sizing or varnish similar to that which painters use for applying gold leaf. "Fat oil"—i. e., partly oxidized linseed oil, supplied by paint dealers—proved very satisfactory for this purpose. While this sizing is still sticky, the dry pigment is dusted on with a camel's hair brush. After the varnish has set the excess of pigment is wiped off and the crucible is fired at a strong red heat, preferably in a muffle. The "fat oil" dries slowly. This is an advantage because then some time may be allowed between its application and the dusting on of the pigment for the irregular layer on the porcelain to draw out by surface tension into a smoother one. Standing overnight at room temperature, or for one hour in a drying oven at 100° C., suffices for the varnish to set. The pad used for "inking" the type may consist of several thicknesses of linen cloth and is nearly saturated with this varnish. Too much varnish on the pad must be avoided, as it results in figures with ragged outlines. This varnish may readily be cleaned from the rubber type before it has set by use of a 10 per cent alcoholic solution of caustic potash applied with a small bristle brush.

COLOR TESTS.

Seeking a prominent color and one resistant to both acids and alkalis, a series of tests was made with samples of overglaze blues, blacks, and reds supplied by a dealer and one blue prepared by the writer. These were stamped onto porcelain crucibles as above described. The heat used in firing was a red heat slightly lower than that at which the colored figures on the white background disappeared (the radiation plus reflection from a colored surface equaling that from a white surface). In one test they were brought from a dull red to the above temperature during the course of one hour and then cooled. This sufficed to make the blacks and the reds resistant to nitric acid (35 per

cent) and to sodium-hydroxide solution (10 per cent), but the blues were appreciably soluble in the acid. To make the blues resistant, they had to be fired to a higher temperature or held at the above maximum temperature for about an hour. To test the permanence of the markings, the acid and the alkali were each applied five minutes cold, followed by five minutes at a boiling temperature. Of the seven blacks tried, two—viz., a lettering black and a blue black—gave especially good effects in that they yielded a very strong black. Of the same samples when applied to silica dishes and fired as indicated both the blacks and the reds were again resistant to both nitric acid and alkali, but the blues, even when fired more strongly, came off very readily in nitric acid.

In these tests an electric muffle was used. In heating porcelain crucibles to a high temperature in gas muffles in which the muffle chambers were not thoroughly sealed off from the gas chambers, and occasionally also in the electric muffle, a brown stain developed on the porcelain. This could readily be removed by heating the crucible half a minute in the blast flame, most conveniently in a suitable chimney.

In applying the rubber stamp to the crucibles it is difficult to avoid a sliding motion that blurs the imprint. This may be prevented by using a suitable guide or a steadying support. Mr. Yoder found it convenient to rest both the inverted crucible and the type holder on a smooth surface while making the impression. In numbering crucibles, etc., it is often advantageous to have the number on three sides so as to make it visible, no matter which way the crucible is turned.

A recent consular report states that the exportation of guano from Mexico through the Port of Mo-gales amounted to 1,893 tons for the fiscal year ending June 30, 1911. This is always bat guano and is found in various localities all over the state of Sonora and in fact all along the northwest coast of Mexico, where in recent years various concessions have been granted for its exploitation. It is usually found in caves in the mountains, where it is gathered into sacks and carried on burros to the nearest railway station and shipped to fertilizer works in California. The price given in consular invoices and shown on export returns is merely an estimate, as the guano is shipped on consignment to the fertilizer works, where a chemical analysis is made. The price paid the shipper depends on the amount of ammonia contained. Guano, which contains less than 10 per cent ammonia will not be accepted. While occasional shipments run as high as 20 per cent, the average is from 12 to 15 per cent. A crude manner of determining whether the percentage of ammonia is large enough to pay for shipping is followed. The guano is mixed with a little unslacked lime and water in a small receptacle, and from the ammonia fumes which arise the guano hunter judges whether the deposit will pay for the handling.

A NEW METHOD FOR THE DETERMINATION OF THE REDUCING SUGARS.*

A desire to determine reducing sugars resulting from the digestion of starch with the greatest possible accuracy led the author to study some modifications of Fehling's reagent with a view to establishing the optimum medium.

It has been pointed out¹ that NaOH destroys glucose more readily than Na_2CO_3 . Results are given: 50 mgm. glucose reduces:

Deiren's method	89.8 Mgm.
Allibu's method	98.2 Mgm.
Munsen and Walker's method.....	102.0 Mgm.
Na_2CO_3 sol. replacing NaOH.....	147 Mgm.

After series of experiments, K_2CO_3 was found to be the best solution to furnish the alkalinity, as it is more soluble than Na_2CO_3 and gives slightly more copper reduced for the same weight of glucose. Results are given.

Having a medium for alkalinity, the next step was to determine if there was a better medium than Rochelle salts for holding the copper in solution. With tartrate, spontaneous reducing power of the solution must be allowed for. Author gives figures on boiling ordinary solutions, filtering off Cu_2O and obtaining almost an equal weight on a second and third boiling. This showed that reduction is due to tartrate itself and not to impurities.

Other solutions than tartrate have been tried. Results are given with sodium citrate showing a variation with weight of citrate not following a definite law. Results were also very low and make citrate out of the question.

Glycerol and mannite, lactic acid and others were suggested, tried and found unsatisfactory. Of all those possible, salicylic acid gave the best results. The proper amounts and conditions remained to be determined.

An alkaline salicylate solution with Cu SO_4 solution showed no reduction of copper when heated with boiling water 7 hours. Slight increases in amount of salicylic acid showed little change in weight of copper reduced. Results given. Favorable results also obtained with other sugars, results given showing that 15 gms. K_2CO_3 , 5 gms. salicylic acid and 2 gms. Cu SO_4 in a total volume of 140 cc. form most satisfactory quantity. Cu and K salicylate were too insoluble to dissolve in this quantity, so K_2CO_3 and Cu SO_4 were dissolved separately in water and salicylic acid added after other two to sugar solution.

Results are given with different methods of heating showing boiling water to be best and most convenient. Results given on time of heating: 20 minutes found to almost complete reaction and be most convenient for running consecutive determinations. Experiment showed it impossible to replace salicylic acid by sodium salicylate and also that it was necessary to add the potassium-copper salicylate to the sugar solution and

*Abstracted from Jour. Am. Chem. Soc., Vol. 34, No. 3, p. 317, by E. W. McMullen.

¹Benedict, J., Biol. Chem. 3, 101 (1907); 5, 485 (1908).

not vice versa. Results also show that mixture standing over 5 to 6 minutes before boiling causes changes in the reducing power of the sugar. Temperature of solutions before boiling makes little difference between 18° and 50°. Slight differences in the weights of K_2CO_3 and salicylic acid present were shown by experiment to give little difference in Cu_2O .

Copper determined in Cu_2O by dissolving from Gooch with 10 cc. hot nitric acid (1:3) from wash bottle, then with hot water. Copper determined in the solution by a modification of the iodide method².

Pure sugars were prepared by standard methods to determine the ratio of Cu_2O to reducing sugar. The method follows:

Copper sulphate solution: Dissolve 133.33 gms. $CuSO_4 \cdot 5H_2O$ in a liter of water; 15 cc. contains 2 gms. $CuSO_4$.

Pot. carbonate solution: Dissolve 600 gm. anhydrous K_2CO_3 in a liter of water. Ordinary K_2CO_3 must be heated to 190° to 200° for 3 or 4 hours to lose all its moisture; 25 cc. contains 15 gms. K_2CO_3 .

To the sugar solution containing less than .450 gm. sugar add sufficient water to make 100 cc. Use a 250 cc. Erlenmeyer. Add 5.0 gms. salicylic acid, 15 cc. $CuSO_4$ solution and 25 cc. K_2CO_3 solution in this order. Rotate till precipitate dissolves. Place in water bath of 4 liters' capacity with water boiling vigorously. Flame should be such that boiling starts 1.5 to 2 minutes after addition of flasks. Results are given for various sugars. Ratios between Cu and sugar determined by method of least squares and following equations deduced:

X = weight of copper reduced. Y = weight of sugar reacting.

Glucose $X = -0.17 + 3.0023Y - 0.002026Y^2$

Invert sugar..... $X = -1.30 + 3.2918Y - 0.002455Y^2$

Lactose $X = -0.50 + 1.5786Y - 0.000217Y^2$

Maltose $X = -1.60 + 1.5988Y - 0.000187Y^2$

Results are given showing differences between calculations and results which are slight.

Determinations were made from 10 to 160 mg. varying by 2 mg. for glucose and invert sugars. Complete tables for glucose, invert sugar, lactose and maltose were found from 10 to 450 mgm. sugar and were interpolated to vary by 1.0 mgm. Cu . Cu_2O and CuO values are also given in the following table:

TABLE OF COPPER REDUCED BY SUGARS.

TABLE OF COPPER REDUCED BY SUGARS.						
Copper, Mgm.	Cuprous oxide, Mgm.	Cupric oxide, Mgm.	Glucose, Mgm. $C_6H_{12}O_6$	Invert sugar, Mgm. $C_6H_{12}O_6$	Lactose, Mgm. $C_6H_{12}O_6 \cdot H_2O$	Maltose, Mgm. $C_6H_{12}O_6 \cdot H_2O$
30	33.8	37.6	9.8	9.6	19.3	19.9
31	34.9	38.8	10.2	9.9	20.6	20.5
32	36.0	40.1	10.5	10.2	20.6	21.1
33	37.2	41.3	10.8	10.5	21.2	21.7
34	38.3	42.6	11.1	10.8	21.8	22.4
35	39.4	43.8	11.5	11.1	22.5	23.0
36	40.5	45.1	11.8	11.4	23.1	23.6
37	41.7	46.3	12.1	11.8	23.7	24.3
38	42.8	47.6	12.4	12.1	24.4	24.9
39	43.9	48.8	12.8	12.4	25.0	25.5
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Jour. Am. Chem. Soc., 33, 1947.

²Jour. Am. Chem. Soc., 33, 1947.

Copper, Mgm.	Cuprous oxide, Mgm.	Cupric oxide, Mgm.	Glucose, Mgm. $C_6H_{12}O_6$	Invert sugar, Mgm. $C_6H_{12}O_6$	Lactose, Mgm. $C_{12}H_{22}O_{11}H_2O$	Maltrose, Mgm. $C_{12}H_{22}O_{11}H_2O$	Copper, Mgm.	Cuprous oxide, Mgm.	Cupric oxide, Mgm.	Glucose, Mgm. $C_6H_{12}O_6$	Invert sugar, Mgm. $C_6H_{12}O_6$	Lactose, Mgm. $C_{12}H_{22}O_{11}H_2O$	Maltrose, Mgm. $C_{12}H_{22}O_{11}H_2O$
121	136.2	151.5	40.3	38.3	77.1	77.4	202	227.4	252.8	68.5	64.9	129.9	129.4
122	137.4	152.7	40.6	38.6	77.7	78.1	203	228.5	254.0	68.7	65.2	130.6	130.0
123	138.5	154.0	40.9	38.9	78.4	78.7	204	229.7	255.3	69.2	65.6	131.2	130.6
124	139.6	155.2	41.3	39.2	79.0	79.4	205	230.8	256.5	69.5	65.9	131.9	131.3
125	140.7	156.5	41.6	39.5	79.7	80.0	206	231.9	257.8	69.9	66.2	132.5	131.9
126	141.9	157.7	42.0	39.9	80.3	80.6	207	233.0	259.0	70.2	66.6	133.2	132.6
127	143.0	159.0	42.3	40.2	81.0	81.3	208	234.2	260.3	70.6	66.9	133.8	133.2
128	144.1	160.2	42.6	40.5	81.6	81.9	209	235.3	261.5	71.0	67.3	134.5	133.9
129	145.2	161.5	43.0	40.8	82.3	82.5	210	236.4	262.8	71.3	67.6	135.2	134.5
130	146.4	162.7	43.3	41.2	82.9	83.2	211	237.6	264.0	71.7	67.9	135.8	135.2
131	147.5	164.0	43.7	41.5	83.6	83.8	212	238.7	265.3	72.0	68.3	136.5	135.8
132	148.6	165.2	44.0	41.8	84.2	84.5	213	239.8	266.5	72.4	68.6	137.1	136.5
133	149.7	166.5	44.4	42.1	84.9	85.2	214	240.9	267.8	72.7	69.0	137.8	137.1
134	150.9	167.7	44.7	42.5	85.5	85.8	215	242.1	269.0	73.1	69.3	138.5	137.8
135	152.0	169.0	45.1	42.8	86.2	86.5	216	243.2	270.3	73.4	69.6	139.1	138.4
136	153.1	170.2	45.4	43.1	86.8	87.1	217	244.3	271.5	73.8	70.0	139.8	139.1
137	154.2	171.5	45.7	43.4	87.4	87.7	218	245.4	272.8	74.2	70.3	140.4	139.7
138	155.4	172.7	46.1	43.8	88.1	88.3	219	246.6	274.1	74.5	70.7	141.1	140.3
139	156.5	174.0	46.4	44.1	88.7	88.9	220	247.7	275.4	74.9	71.0	141.8	141.0
140	157.6	175.2	46.8	44.4	89.4	89.6	221	248.7	276.6	75.2	71.4	142.4	141.6
141	158.7	176.5	47.1	44.7	90.0	90.2	222	249.9	277.9	75.6	71.7	143.1	142.3
142	159.9	177.7	47.5	45.1	90.7	90.8	223	251.0	279.1	76.0	72.0	143.7	142.9
143	161.0	179.0	47.8	45.4	91.3	91.5	224	252.1	280.4	76.3	72.4	144.4	143.6
144	162.1	180.2	48.1	45.7	92.0	92.1	225	253.3	281.6	76.7	72.7	145.1	144.2
145	163.2	181.5	48.5	46.0	92.6	92.8	226	254.4	282.9	77.0	73.1	145.7	144.9
146	164.4	182.7	48.8	46.4	93.3	93.4	227	255.6	284.1	77.4	73.4	146.4	145.5
147	165.5	184.0	49.2	46.7	93.9	94.0	228	256.7	285.4	77.8	73.7	147.0	146.2
148	166.6	185.2	49.5	47.0	94.6	94.7	229	257.8	286.6	78.1	74.1	147.7	146.8
149	167.7	186.5	49.9	47.4	95.3	95.3	230	258.9	287.9	78.5	74.4	148.4	147.5
150	168.9	187.8	50.2	47.7	95.9	96.0	231	260.1	289.1	78.8	74.8	149.0	148.1
151	170.0	189.0	50.6	48.0	96.6	96.6	232	261.2	290.4	79.2	75.1	149.7	148.8
152	171.1	190.3	50.9	48.3	97.2	97.2	233	262.3	291.6	79.6	75.4	150.3	149.4
153	172.3	191.5	51.3	48.7	97.9	97.9	234	263.4	292.9	79.9	75.8	151.0	150.1
154	173.4	192.8	51.6	49.0	98.5	98.5	235	264.6	294.1	80.3	76.1	151.7	150.7
155	174.5	194.0	52.0	49.3	99.2	99.2	236	265.7	295.4	80.6	76.5	152.3	151.4
156	175.6	195.3	52.3	49.6	99.8	99.8	237	266.8	296.6	81.0	76.8	153.0	152.0
157	176.8	196.5	52.7	50.0	100.5	100.4	238	268.0	297.9	81.4	77.2	153.6	153.6
158	177.9	197.8	53.0	50.3	101.1	101.1	239	269.1	299.1	81.7	77.5	154.3	153.3
159	179.0	199.0	53.4	50.6	101.8	101.7	240	270.2	300.4	82.1	77.8	155.0	153.9
160	180.1	200.3	53.7	50.9	102.4	102.4	241	271.3	301.6	82.5	78.2	155.6	154.6
161	181.3	201.5	54.0	51.3	103.1	103.0	242	272.5	302.9	82.8	78.5	156.3	155.2
162	182.4	202.8	54.4	51.6	103.7	103.6	243	273.6	304.1	83.2	78.9	157.0	155.9
163	183.5	204.0	54.7	51.9	104.4	104.3	244	274.7	305.4	83.5	79.2	157.6	156.5
164	184.6	205.3	55.1	52.3	105.0	104.9	245	275.8	306.6	83.9	79.6	158.3	157.2
165	185.8	206.5	55.4	52.6	105.7	105.6	246	277.0	307.9	84.3	79.9	159.0	157.8
166	186.9	207.8	55.8	52.9	106.3	106.2	247	278.1	309.1	84.6	80.2	159.6	158.5
167	188.0	209.0	56.1	53.3	107.0	106.8	248	279.2	310.4	85.0	80.6	160.3	159.1
168	189.1	210.3	56.5	53.6	107.6	107.5	249	280.3	311.6	85.4	80.9	160.9	159.8
169	190.3	211.5	56.8	53.9	108.3	108.1	250	281.5	312.9	85.7	81.3	161.6	160.4
170	191.4	212.8	57.2	54.2	108.9	108.8	251	282.6	314.1	86.1	81.6	162.2	161.1
171	192.5	214.0	57.5	54.6	109.6	109.4	252	283.7	315.4	86.5	82.0	162.9	161.7
172	193.6	215.3	57.9	54.9	110.2	110.1	253	284.8	316.6	86.8	82.3	163.6	162.4
173	194.8	216.5	58.2	55.2	110.9	110.7	254	286.0	317.9	87.2	82.7	164.2	163.0
174	195.9	217.8	58.6	55.6	111.6	111.3	255	287.1	319.1	87.6	83.0	164.9	163.7
175	197.0	219.0	58.9	55.9	112.2	112.0	256	288.2	320.4	87.9	83.4	165.6	164.3
176	198.1	220.3	59.3	56.2	112.9	112.6	257	289.3	321.6	88.3	83.7	166.2	165.0
177	199.3	221.5	59.6	56.6	113.5	113.3	258	290.5	322.9	88.7	84.1	166.9	165.6
178	200.4	222.8	60.0	56.9	114.2	113.9	259	291.6	324.1	89.0	84.4	167.6	166.3
179	201.5	224.0	60.3	57.2	114.9	114.5	260	292.7	325.4	89.4	84.8	168.2	166.9
180	202.6	225.3	60.7	57.6	115.5	115.2	261	293.8	326.6	89.8	85.1	168.9	167.6
181	203.8	226.5	61.0	57.9	116.1	115.8	262	295.0	327.9	90.1	85.5	169.5	168.3
182	204.9	227.8	61.4	58.2	116.8	116.5	263	296.1	329.1	90.5	85.8	170.2	168.9
183	206.0	229.0	61.7	58.6	117.4	117.1	264	297.2	330.4	90.8	86.1	170.9	169.6
184	207.1	230.3	62.1	58.9	118.1	117.8	265	298.3	331.6	91.2	86.5	171.6	170.2
185	208.3	231.5	62.4	59.2	118.8	118.4	266	299.5	332.9	91.6	86.8	172.2	170.9
186	209.4	232.7	62.8	59.6	119.4	119.0	267	300.6	334.1	91.9	87.2	172.9	171.5
187	210.5	234.0	63.1	59.9	120.1	119.7	268	301.7	335.4	92.3	87.5	173.5	172.2
188	211.7	235.3	63.5	60.2	120.7	120.3	269	302.8	336.7	92.7	87.9	174.2	172.8
189	212.8	236.5	63.9	60.6	121.4	121.0	270	304.0	338.0	93.1	88.2	174.9	173.5
190	213.9	237.8	64.2	60.9	122.0	121.6	271	305.1	339.2	93.4	88.6	175.5	174.1
191	215.0	239.0	64.6	61.2	122.7	122.3	272	306.2	340.5	93.8	88.9	176.2	174.8
192	216.2	240.3	64.9	61.6	123.3	122.9	273	307.3	341.7	94.2	89.3	176.9	175.4
193	217.3	241.5	65.3	61.9	124.0	123.6	274	308.5	343.0	94.5	89.6	177.5	176.1
194	218.4	242.8	65.6	62.2	124.7	124.2	275	309.6	344.2	94.9	90.0	178.2	176.7
195	219.5	244.0	66.0	62.6	125.3	124.8	276	310.7	345.5	95.3	90.3	178.9	177.4
196	220.7	245.3	66.3	62.9	126.0	125.5	277	311.9	346.7	95.6	90.7	179.5	178.0
197	221.8	246.5	66.7	63.2	126.6	126.1	278	313.0	348.0	96.0	91.1	180.2	178.7
198	222.9	247.8	67.0	63.6	127.3	126.8	279	314.1	349.2	96.4	91.4	180.9	179.3
199	224.0	249.0	67.4	63.9	127.9	127.4	280	315.2	350.5	96.7	91.8	181.5	180.0
200	225.2	250.3	67.8	64.2	128.6	128.1	281	316.4	351.7	97.1	92.1	182.2	180.6
201	226.3	251.5	68.1	64.6	129.2	128.7	282	317.5	353.0	97.5	92.5	182.9	181.3

	Copper. Mgm.	Cuprous oxide. Mgm.	Cupric oxide. Mgm.	Glucose. Mgm. $C_6H_{12}O_6$.	Invert sugar. Mgm. $C_6H_{12}O_6$.	Lactose. Mgm. $C_{12}H_{22}O_{11}.H_2O$.	Maltose. Mgm. $C_{12}H_{22}O_{11}.H_2O$.	Copper. Mgm.	Cuprous oxide. Mgm.	Cupric oxide. Mgm.	Glucose. Mgm. $C_6H_{12}O_6$.	Invert sugar. Mgm. $C_6H_{12}O_6$.	Lactose. Mgm. $C_{12}H_{22}O_{11}.H_2O$.	Maltose. Mgm. $C_{12}H_{22}O_{11}.H_2O$.
273	318.6	354.2	97.9	92.8	183.5	181.9	364	409.8	455.6	128.6	122.1	238.0	235.2	235.2
274	319.7	355.5	98.2	93.1	184.2	182.6	365	410.9	456.9	129.0	122.5	238.7	235.9	235.9
285	320.9	356.7	98.6	93.5	184.9	183.2	366	412.1	458.1	129.4	122.9	239.4	236.5	236.5
286	322.0	358.0	99.0	93.9	185.5	183.9	367	413.2	459.4	129.8	123.2	240.1	237.2	237.2
287	323.1	359.2	99.4	94.2	186.2	184.6	368	414.3	460.6	130.2	123.6	240.7	237.8	237.8
288	324.2	360.5	99.7	94.6	186.9	185.2	369	415.4	461.9	130.6	124.0	241.4	238.5	238.5
289	325.3	361.7	100.1	94.9	187.6	185.9	370	416.6	463.1	131.0	124.3	242.1	239.2	239.2
290	326.4	363.0	100.5	95.3	188.2	186.5	371	417.7	464.4	131.4	124.7	242.8	239.8	239.8
291	327.5	364.2	100.8	95.6	188.8	187.2	372	418.8	465.6	131.8	125.1	243.5	240.5	240.5
292	328.7	365.5	101.2	96.0	189.5	187.8	373	420.0	466.9	132.1	125.5	244.1	241.2	241.2
293	329.9	366.7	101.6	96.3	190.1	188.5	374	421.1	468.1	132.5	125.8	244.8	241.8	241.8
294	331.0	368.0	101.9	96.7	190.8	189.1	375	422.2	469.4	132.9	126.2	245.5	242.5	242.5
295	332.1	369.2	102.3	97.1	191.4	189.8	376	423.3	470.6	133.3	126.6	246.2	243.1	243.1
296	333.3	370.5	102.7	97.4	192.1	190.4	377	424.5	471.9	133.7	127.0	246.8	243.8	243.8
297	334.4	371.7	103.1	97.8	192.8	191.1	378	425.6	473.0	134.1	127.4	247.5	244.5	244.5
298	335.5	373.0	103.4	98.1	193.5	191.8	379	426.7	474.3	134.5	127.7	248.2	245.1	245.1
299	336.6	374.2	103.8	98.5	194.2	192.4	380	427.8	475.6	134.9	128.1	248.9	245.8	245.8
300	337.8	375.5	104.2	98.9	194.9	193.1	381	429.0	476.8	135.3	128.5	249.6	246.5	246.5
301	338.9	376.7	104.6	99.2	195.6	193.7	382	430.1	478.1	135.7	128.8	250.2	247.1	247.1
302	340.0	378.0	105.0	99.6	196.2	194.4	383	431.2	479.3	136.1	129.2	250.9	247.8	247.8
303	341.1	379.2	105.3	99.9	196.9	195.0	384	432.3	480.6	136.5	129.6	251.6	248.5	248.5
304	342.3	380.5	105.7	100.3	197.6	195.7	385	433.5	481.8	136.9	130.0	252.3	249.1	249.1
305	343.4	381.7	106.1	100.6	198.3	196.3	386	434.6	483.1	137.3	130.3	253.0	249.8	249.8
306	344.5	383.0	106.4	101.0	198.9	197.0	387	435.7	484.3	137.7	130.7	253.6	250.4	250.4
307	345.6	384.2	106.8	101.3	199.6	197.6	388	436.8	485.6	138.0	131.1	254.3	251.1	251.1
308	346.8	385.5	107.2	101.7	200.3	198.3	389	438.0	486.9	138.4	131.5	255.0	251.8	251.8
309	347.9	386.7	107.6	102.1	200.9	199.0	390	439.1	488.2	138.8	131.9	255.7	252.4	252.4
310	349.0	388.0	107.9	102.4	201.6	199.6	391	440.2	489.4	139.2	132.2	256.4	253.1	253.1
311	350.1	389.2	108.3	102.8	202.3	200.3	392	441.3	490.7	139.6	132.6	257.0	253.8	253.8
312	351.3	390.5	108.7	103.1	202.9	200.9	393	442.4	491.9	140.0	133.0	257.7	254.4	254.4
313	352.4	391.7	109.1	103.5	203.6	201.6	394	443.6	493.2	140.4	133.4	258.4	255.1	255.1
314	353.5	393.0	109.5	103.8	204.3	202.2	395	444.7	494.4	140.8	133.8	259.1	255.8	255.8
315	354.6	394.2	109.8	104.2	204.9	202.9	396	445.9	495.7	141.2	134.2	259.8	256.4	256.4
316	355.8	395.5	110.2	104.6	205.5	203.6	397	447.0	496.9	141.6	134.5	260.5	257.1	257.1
317	356.9	396.7	110.6	104.9	206.2	204.2	398	448.1	498.2	142.0	134.9	261.1	257.8	257.8
318	358.0	398.0	111.0	105.3	206.8	204.9	399	449.2	499.5	142.4	135.2	261.8	258.4	258.4
319	359.1	399.2	111.4	105.6	207.5	205.5	400	450.3	500.7	142.8	135.7	262.5	259.1	259.1
320	360.3	400.5	111.7	106.0	208.2	206.2	401	451.5	502.0	143.2	136.1	263.2	259.8	259.8
321	361.4	401.7	112.1	106.4	208.9	206.8	402	452.6	503.2	143.6	136.4	263.9	260.4	260.4
322	362.5	403.0	112.5	106.7	209.6	207.5	403	453.7	504.5	144.0	136.8	264.5	261.1	261.1
323	363.7	404.2	112.9	107.1	210.3	208.2	404	454.8	505.7	144.4	137.2	265.2	261.8	261.8
324	364.8	405.5	113.2	107.5	211.0	208.8	405	456.0	507.0	144.8	137.6	265.9	262.4	262.4
325	365.9	406.7	113.6	107.8	211.7	209.5	406	457.1	508.2	145.2	137.9	266.6	263.1	263.1
326	367.0	408.0	114.0	108.2	212.3	210.1	407	458.2	509.5	145.6	138.3	267.3	263.8	263.8
327	368.2	409.2	114.4	108.5	213.0	210.8	408	459.4	510.7	146.0	138.7	267.9	264.4	264.4
328	369.3	410.5	114.8	108.9	213.6	211.5	409	460.5	512.0	146.4	139.1	268.6	265.1	265.1
329	370.4	411.8	115.1	109.3	214.3	212.1	410	461.6	513.2	146.8	139.5	269.3	265.8	265.8
330	371.5	413.1	115.5	109.6	214.9	212.8	411	462.7	514.5	147.2	139.9	270.0	266.4	266.4
331	372.7	414.3	115.9	110.0	215.6	213.4	412	463.8	515.7	147.6	140.2	270.7	267.1	267.1
332	373.8	415.6	116.3	110.3	216.3	214.1	413	465.0	517.0	148.0	140.6	271.4	267.8	267.8
333	374.9	416.8	116.7	110.7	217.0	214.7	414	466.1	518.2	148.4	141.0	272.1	268.4	268.4
334	376.0	418.1	117.0	111.1	217.7	215.4	415	467.2	519.5	148.8	141.4	272.8	269.1	269.1
335	377.2	419.3	117.4	111.5	218.4	216.1	416	468.4	520.7	149.2	141.8	273.5	269.7	269.7
336	378.3	420.6	117.8	111.8	219.1	216.7	417	469.5	522.0	149.6	142.2	274.1	270.4	270.4
337	379.4	421.9	118.2	112.2	219.8	217.4	418	470.6	523.2	150.0	142.6	274.8	271.1	271.1
338	380.5	423.1	118.6	112.5	220.4	218.0	419	471.8	524.5	150.4	143.0	275.5	271.8	271.8
339	381.7	424.4	119.0	112.9	221.1	218.7	420	472.9	525.7	150.8	143.3	276.2	272.4	272.4
340	382.8	425.6	119.4	113.3	221.7	219.3	421	474.0	527.0	151.2	143.7	276.9	273.1	273.1
341	383.9	426.9	119.8	113.6	222.4	220.0	422	475.1	528.2	151.6	144.1	277.6	273.8	273.8
342	385.0	428.1	120.1	114.0	223.0	220.7	423	476.2	529.5	152.0	144.5	278.3	274.4	274.4
343	386.2	429.4	120.5	114.4	223.7	221.3	424	477.4	530.7	152.4	144.9	278.9	275.1	275.1
344	387.3	430.6	120.9	114.7	224.4	222.0	425	478.5	532.0	152.8	145.3	279.6	275.8	275.8
345	388.4	431.9	121.3	115.1	225.1	222.6	426	479.6	533.2	153.2	145.7	280.3	276.5	276.5
346	389.6	433.1	121.7	115.5	225.8	223.3	427	480.7	534.5	153.6	146.1	280.9	277.1	277.1
347	390.7	434.4	122.1	115.8	226.5	224.0	428	481.9	535.7	154.0	146.4	281.6	277.8	277.8
348	391.8	435.6	122.4	116.2	227.2	224.6	429	483.0	537.0	154.4	146.8	282.3	278.5	278.5
349	392.9	436.9	122.8	116.6	227.9	225.3	430	484.1	538.2	154.8	147.2	282.9	279.1	279.1
350	394.0	438.1	123.2	117.0	228.5	225.9	431	485.3	539.5	155.2	147.6	283.6	279.8	279.8

Copper, Mgm.	Cuprous oxide Mgm.	Cupric oxide, Mgm.	Glucose, Mgm. $C_6H_{12}O_6$	Invert sugar, Mgm. $C_6H_{12}O_6$	Lactose, Mgm. $C_6H_{12}O_6 \cdot nH_2O$	Maltose, Mgm. $C_6H_{12}O_6 \cdot nH_2O$
445	501.0	557.0	161.0	153.1	293.4	289.2
446	502.1	558.2	161.4	153.5	294.1	289.8
447	503.2	559.5	161.8	153.9	294.8	290.5
448	504.4	560.7	162.2	154.3	295.5	291.2
449	505.5	562.0	162.6	154.7	296.2	291.9
450	506.6	563.3	163.0	155.1	296.9	292.5

The total production of pig iron in Germany in 1911, according to statistics collected by the Association of German Iron and Steel Producers amounted to metric 15,534,223 tons, as contrasted with 14,793,325 tons in the preceding year, or an increase of 74,898 tons. It is of some interest to note that, owing chiefly to the development of the "minette" iron ore resources in Lorraine and Luxemburg in the past few years, and more recently to the growing importation of similar ore from the Meurthe and Moselle district in the east of France, the production of pig iron in Germany has doubled since 1901, when the output of pig iron only totaled 7,880,000 tons. A further very considerable growth in the manufacture of pig iron in Germany may be expected in the course of the next few years, beginning with the present year. Apart from the erection of new blast furnaces in connection with existing iron and steel works, three entirely new iron and steel works of enormous dimensions are approaching completion in Lorraine-Luxemburg at Hagendingen and Esch, and these alone will have a total annual capacity of about 1,600,000 tons of pig iron. The increase in the productive capacity for the whole of the country will be about 5,000,000 tons in from three to four years from the present time, and the only question is as to where a market will be found for the enormous expansion in the output, although this matter does not appear to cause any concern to the owners of the new works or the promoters of two other large new works. At any rate, the tonnage of pig iron which can not be placed on the market in the form of manufactured steel will be marketed both in Germany and abroad, and a fund of nearly \$200,000 per annum for the forcing of the export trade is already proposed to be formed by the Pig-Iron-Syndicate for utilization in case of necessity.

Minister Nicolay A. Grevstad, of Montevideo, reports the successful result of an official test, in Buenos Aires, of a new Argentine process of preserving meats, fish, and vegetables. He states that the invention, which is patented, consists in the preparation of a fluid that may be used by the housewife as well as in large establishments. The commission which made the official test states: "As the chemical analysis has not revealed the presence of any antiseptic or any other substance injurious to health, it may be concluded that meat and fish treated in this manner are perfectly adapted for food."

THE ARSENIC CONTENT OF SHELLAC AND THE CONTAMINATION OF FOODS FROM THIS SOURCE.*

By BERNARD H. SMITH.

Orpiment, the yellow sulphur of arsenic, is very generally added to shellac in India for the purpose of rendering the product opaque and at the same time producing the light-straw color characteristic of the higher grades. This is of interest to the food chemist, the health official, and the consumer, for shellac is used as a coating for certain food products, such as some kinds of confectionery and bakers' products, and is largely used as a varnish on receptacles and containers of various kinds in many lines of food manufacture. Rosin is said to be added to lower the melting point, which is of advantage to some industries. It is also much cheaper than shellac.

The addition of mineral coloring matters to shellac has long been practiced. Van Linschoten, who is reported to have been sent to India by Portugal, stated in 1596 that "when the lac is raw, as it cometh from the tree, it is a darke red colour, but being refined and cleansed they make it of all colours of India." Baden-Powell, in his handbook of "The Manufactures and Arts of the Panjab," in discussing the manufacture of laquered ware, writes: "Mineral colors are mostly used. The yellow is made with orpiment; green with arsenite of copper; red with red lead or vermilion; blue with imitation 'lájward' or Prussian blue." The addition of orpiment to shellac, as well as rosin, is discussed in some detail by Watt,¹ who says in part: "According to the particular class of manufacture desired lac is now very often mixed with either or both of the following substances, namely, orpiment or yellow arsenic and resin. The latter is obtained for the most part from Canada (pine rosin). The former is procured in India and apparently serves mainly (if not entirely) a mechanical purpose. It makes the lac opaque, but at the same time imparts to it a rich pale straw color, properties characteristic of all the finer grades of handmade shellac. Arsenic is not, however, employed in the manufacture of 'garnet,' 'button,' and the other grades where paleness of color is not so much demanded. * * * During seasons of high prices the admixture of rosin is often raised until it passes from the condition of permissible admixture to what might be called criminal adulteration."

Shellac has been used by many of the larger confectioners to the extent of several barrels a month each primarily for the purpose of giving the goods so treated a gloss or high finish and a superior appearance. The amount of dry shellac on these candies varies from a small fraction of a per cent to 1.5 per cent, depending on the amount of surface exposed and the thickness of the coating. Penny goods and those usually consumed by children, such as fudge of various kinds, peanut bars, sugar-coated peanuts, imitation

*Circular U. S. Bureau of Chemistry.

chocolate cigars, etc., are more often shellacked than other classes of confectionery.

Orpiment is not readily soluble. In fact, it is nearly insoluble in alcohol, which is ordinarily used as the vehicle of shellac, and a yellow deposit of the arsenical compound tends to settle to the bottom, which concentrates the arsenic in the dregs of each container, so that a larger amount is applied to the articles last varnished.

When used as a coating for food receptacles the insolubility of orpiment and the shellac itself prevents any great amount of the former from going into solution, but several samples of beer and ale from different

retail packages, especially those of ale, are also usually shellacked; and while the amount of arsenic imparted to the fermented beverages from this source is undoubtedly small this easily avoidable trace is added to any that may be present from the materials of the brew, and it should be remembered that arsenic is a cumulative poison and that the beer drinker consumes liberal quantities at not infrequent intervals.

In Table I is shown the quantity of arsenic found in samples of shellac purchased at random on the open market, the duplicated samples of the same mark being obtained from different dealers. The brewers' shellacs, a majority of which were cut in denatured alcohol, were obtained direct from the breweries. The arsenic as reported is calculated to the dry material.

The data show that all of the samples examined contained arsenic. Several alternatives are open to the food manufacturer who wishes to reduce the possibility of arsenical contamination from this source to a minimum. Foreign shippers state that a shellac free from arsenic and rosin may be procured if specially manufactured. Bleached shellac usually contains much less arsenic than unbleached shellac because of the washing to which it is subjected after bleaching. The grades known as "button" and "garnet" contain but small amounts of arsenic, judging from the analyses reported and the statement of Watt,¹ these probably being due to accidental contamination. In the case of the brewer the "glass lined" metallic storage tanks which are rapidly coming into use do away with the need of varnish on these receptacles, which also have the advantage of being very easily cleansed, but the disadvantage of additional cost. Some brewers are using paraffin on all wooden vats, which costs less than shellac, and is reported to give satisfaction.

The addition of orpiment to shellac appears to be wholly unjustifiable, for it works a twofold prejudice to the purchasers of the product: First, to the importer and dealer who judge the quality of the shellac largely by its color and opaqueness, which characteristics are altered by the addition of orpiment. In other words, by the addition of orpiment the manufacturer can sell a shellac of medium or even inferior color and quality as a superior grade. Second, the person using the shellac, in addition to being misled as to its quality, unwittingly uses a product containing arsenic, which, in the case of a manufacturer of foods, is a most serious matter from either an ethical or a commercial viewpoint.

From information collected by the Amur Expedition the amount of gold (in troy ounces) handled by the various gold laboratories in Siberia, in 1910 was as follows: Siberian Bank, Blagoveshtchensk, 330,545; Siberian Bank, Irkutsk, 10,730; Government laboratory, Blagoveshtchensk, 273,534; Government laboratory, Irkutsk, 175,785; Government laboratory, Nicolaevsk, 53,599; total, 844,193.

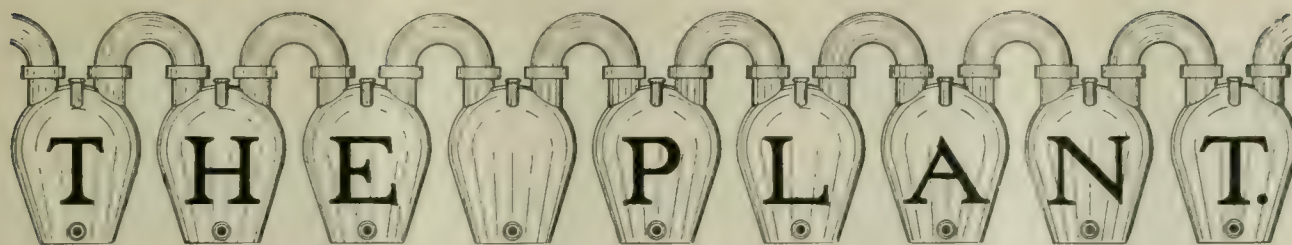
¹Loc. cit.

TABLE I—ARSENIC CONTENT OF SAMPLES OF COMMERCIAL SHELLAC.

No. of sample.	Arsenic as arsenious oxid (parts per million).	Mark.
1.....	225	D. C.
2.....	160	D. C.
3.....	150	D. C.
4.....	700	V. S. O.
5.....	950	V. S. O.
6.....	1,125	Fine Orange.
7.....	260	
8.....	890	
9.....	310	
10.....	525	
11.....	1,430	Ralli Superfine.
12.....	1,280	Standard T. N.
13.....	325	{ L. & M. Pure T. N.
14.....	1,260	{ T. P. K. Pure T. N.
15.....	875	
16.....	40	Button.
17.....	28	A. C. Garnet.
18.....	50	Bleached shellac.
19.....	12	Bleached shellac.
20.....	2,080	Confectioner's shellac.
21.....	4	Arsenic rosin free confectioner's shellac.
22.....	740	Brewer's shellac.
23.....	550	Brewer's shellac.
24.....	520	Brewer's shellac.
25.....	175	Brewer's shellac.
26.....	37	Brewer's shellac.
27.....	32	Brewer's shellac.
28.....	15	Brewer's shellac.

manufacturers, examined by the writer, which were in contact with a coating of shellac, throughout fermentation and aging, all gave strong traces of arsenic.

The brewing industry is a very large user of shellac, the products of many breweries being held in shellac containers from the time the wort leaves the brew kettle, throughout the fermentation and aging processes, until the consumers' glass is drawn "from the wood;" that is, a shellac-lined cask. Fermentation tanks are almost universally shellac varnished, several coats being applied once a year or oftener. Wooden stock tubs and storage tanks, chip casks, and many



CERTAIN PHASES OF TECHNICAL CHEMICAL RESEARCH.

By ARTHUR M. COMEY.

Until within a few years, technical chemical research has received comparatively little attention in this country, although the development of the chemical industries has been very great. In Germany, on the other hand, technical research laboratories have been established and conducted on a large scale for many years and have further developed and increased in size and importance as the German chemical industries have developed. For a long time chemical manufacturers in this country did not realize the advantages of extensive investigation into what seemed to them more or less theoretical questions. It is not difficult to understand the attitude on this question, when we consider that 25 years ago there was hardly a manufacturer who pretended to have any chemical control of works' operations, not to mention the question of research, and some of the most important purely chemical industries did not employ even a single trained chemist. Of late years this condition has greatly changed. The causes for this great development in chemical research laboratories connected with technical operations are undoubtedly complex. One cause, however, which has contributed greatly to this change is the enormous increase in capitalization of various manufacturing industries, making possible the expenditure of considerable sums on laboratories, both in equipment and personnel, and they have found that the establishment of research laboratories on a large scale has been a profitable venture, whereas a small laboratory employing one or two chemists in research work may prove far from a saving investment. The fact must not be overlooked that research laboratories will be maintained for any considerable length of time as a part of the manufacturing costs of a chemical industry, only when they show a real or supposed pecuniary profit. A laboratory may be maintained in isolated cases for a shorter or longer time, when the results obtained therefrom do not pay; but the solid foundation for the continued maintenance of a research laboratory rests on the fact that its operation directly or indirectly increases the profit in the industry with which it is connected.

Manufacturers have been discovering within the last few years that large research laboratories do increase their profits and hence such laboratories are being erected in increasing numbers.

The problem for the small manufacturer is a different one, and many plans have been devised by which he may avail himself of the benefits to be derived from the investigation of problems connected with his industry, without the necessity of establishing a large research laboratory. The usual way to go about this has been for the manufacturer, when he has become convinced that a little research work would help his business, to employ a chemist, just graduated from college, and provide him with a wholly inadequate laboratory, for neither he nor the young chemist has usually any idea of what is necessary in the matter. He then sits back and waits for results. When at the end of six months he not only has not profited several hundred per cent on his research investment, but probably sees no return at all, he is very apt to give the whole matter up and feel that research work in his business at least is a failure. If he had employed a chemist who had already been trained in a large industrial research laboratory and had provided him with the necessary equipment and had had enough confidence in him to wait a reasonable time, it is, in my opinion, most certain that results would be obtained which would warrant the outlay. It is almost impossible, however, that the necessary confidence could be inspired by the ordinary graduate fresh from college.

The situation has been handled recently in a different way by the establishment of industrial fellowships or scholarships in certain of our universities. This scheme has its advantages in removing the necessity of permanently equipping a laboratory, and is undoubtedly more economical as far as the first outlay is concerned. When a comparatively small definite problem is to be worked out, it may be the best solution; but there are many difficulties in the way of extensive use of this manner of industrial research. The difficulty of making sure that the manufacturer who establishes the fellowship should have the whole benefit of the work being not one of the last.

Another serious difficulty in the establishment and continuation of a system of fellowship in a college under one head would arise if the number of these fellowships should become large. The manifold details of the operations involved in each industry which it is necessary for the investigator to understand before he can undertake intelligent research work in that industry would eventually become too overwhelming for any one person to grasp, but it is the plan, as I understand it, that the instructors in charge of the department of the college to which these fellowships are

attached should oversee and direct the work of the men engaged in the actual research, for they were not supposed to be qualified to undertake the research without such direction.

So much for the general subject. I will now take up the rest of my article with a description of the organization of research work in the company with which I am connected, the E. I. duPont deNemours Powder Co. The chemical work of this company is brought together under control of the chemical department. This department occupies the same important position in the company as that held by the engineering department, which has charge of all construction work carried out by the company, and all chemical operations of the company are controlled ultimately by the chemical department. The chemical director occupies a similar position in the organization of the company to that held by the director of the chemical work in the large German companies like the Badische Anilin & Soda Fabrik, for instance. This is as far as I know unique in American industry.

The work of the chemical department is carried on under three distinct divisions. The first division takes charge of those investigations which are made on problems which cannot well be studied in the laboratory. The direction of this work is centered in the main office of the company at Wilmington under one head chemist. In this division are experts on all the various manufacturing activities of the company—nitroglycerine, nitrocotton, sulphuric acid, nitric acid, etc. These are chemists who have usually been trained in our research laboratories, and are engaged in making exhaustive studies on the efficiency of our works operations. These men as I have said have their headquarters at the main office of the company, but often spend long periods of time at the works themselves, where they are assisted by other chemists especially detailed for this work.

Besides the chemists in this division, there is a force of chemists who carry on the routine work of the works laboratories. Each one of our works is equipped with a works laboratory, whereby a close control of works operations is maintained. The chemists engaged in this work are under the control of the superintendents of the various works.

I may mention here that there is a total of about 250 trained chemists in the employ of the duPont Co.

A second division of the chemical department is known as the experimental station. This comprises a laboratory or rather a group of laboratories where research work is carried on on problems connected with the manufacture of smokeless powder and black powder; also problems which are brought to the company from outside are studied here, and from the results obtained the company is in a position to gauge the true value of any process that may be offered them.

The eastern laboratory forms the third division of the chemical organization, and at this laboratory only problems connected in some way with high explosives

are investigated. Under the term "high explosives" are comprised all explosives except black powder and smokeless powder. The term "dynamite" is generally applied to these explosives, but dynamite is a much more comprehensive term than is ordinarily understood by those not acquainted with the explosive industry. The duPont Co., for instance, manufactures at least fifteen different and distinct kinds of dynamite, and of each kind many grades, sometimes as many as ten, representing different strengths. But the point I wish to emphasize is that the work to which the eastern laboratory is devoted concerns not one of the greatest industries in the country, like steel or oil, but one of the lesser industries, and only a branch of that. But in spite of this it has been found to be a distinctly profitable undertaking to maintain a research laboratory on a decidedly large scale. The laboratory organization at the present time is made up as follows: A director, an assistant director, and 25 trained chemists; by trained chemists I mean men who have taken a regular chemical course at a college or scientific school. Among these chemists are several who have taken the degree of Ph.D. here or in Germany. This makes, with the directors, 27 chemists. Besides these we have a professional photographer, whose whole time is devoted to the work of the laboratory, and an office force of six men, including a chief clerk, file clerk, storeroom keepers and stenographers. In addition to the above force, we have about 50 men on our pay roll, making over 80 in all. This list includes three carpenters, three plumbers and pipe fitters, etc., but the majority of these men are ordinary laborers, whom, however, we have trained in many cases to make routine tests, etc.

All the above force are engaged directly or indirectly in the investigations which we are carrying on. The director and assistant director are responsible for the work turned out in the laboratory, but in order to get the best results it is our policy to place a large amount of the direct responsibility upon the chemist who is actually carrying on the research. I believe in this way the best results can be accomplished. The chemist becomes vitally interested in his work when he knows that he is responsible for his results, and in this way the net result to the laboratory is the combined effort of several brains rather than the thoughts of one brain, executed by another's hands. I believe it is of the utmost importance in order to obtain the best results to make a chemist feel that the work is his to carry out, that he is responsible for the results, and that he will receive credit for the results of his work. This cannot be effected if more or less minute directions are given for the details of a research.

Naturally it is imperative under this policy to have first class men, but I believe that the best results can be obtained in a research laboratory only with first class men. Men to whom cannot be trusted the development of a research should not be employed in a research laboratory to carry on researches.

Now I do not wish to convey the idea that, as we have 25 chemists working on research work, we have 25 independent workers or 25 lines of research carried on simultaneously. As a matter of fact, we have about 10 lines of research at the present time, and the men conducting these researches have a number of other chemists to help them in their work. The number of these chemists varies according to the conditions. In some cases it is not necessary for the chemist to have any aid outside of that from the workmen. In other cases there is a large amount of analytical and testing work to do in connection with the research. One of the head research chemists, for instance, has four other chemists working for him. They are under his direction, and only indirectly responsible to the directors of the laboratory. These men, as I said, perform the necessary analytical work and tests connected with the research in question, and besides, these chemists, it is our policy to furnish all the laboring men that the research chemists can profitably employ in their work. This becomes especially important in certain lines of work, as, for instance, the development of a new process in the laboratory. In most cases of this kind, we try the proposed process out on a purely laboratory scale with ordinary laboratory apparatus. If the first results are promising, we may set up a larger apparatus in the laboratory, and then proceed to erect a small experimental plant where the same kind of apparatus is used as is proposed for actual works operation, but on a smaller scale; for instance, experiments on the nitration of glycerine are first carried out in a small laboratory, where 40 grams is used as a charge. Then the operation is repeated at our experimental nitroglycerine plant, where we make about 90 lbs. of nitroglycerine to a charge, instead of many hundred lbs., which is the regular works' scale; but all the apparatus at our small plant is of the same material and practically the same model as that used for actual manufacture.

This development of a process on a semi-manufacturing scale together with the nature of the investigations and their connection with explosives, leads to the necessity of providing a large number of buildings for our work, and you may be interested to know that we have at the present time 76 buildings, spread over about 50 acres of ground, in use in our work at the Eastern Laboratory. The majority of these buildings are of considerable size, and it is customary to carry on only one process or perhaps part of a process in any one building.

The economy of the plan of developing processes to a manufacturing scale under laboratory control is obvious to anyone who has had to do with experimenting at a plant on works' scale. We use our workmen for running these small plants, under the supervision of the chemist who is developing that particular process, and these men often go over to the works when a manufacturing plant is erected for the completed process, and are well trained for operating it.

This plan also helps to keep us in close touch with works' operations, which is a most essential condition in order to make the results of laboratory work most available.

The younger chemists working on the research work under the older men are also being trained, and as the work increases, or our older men are promoted to other positions, they in turn become independent workers, if they are capable of doing such work, which we are able to judge during their term of training. This furnishes a very efficient method for procuring men best adapted to the work to be undertaken.

Another incentive is offered to our chemists to exert their faculties to the utmost in the form of bonuses for unusually meritorious work. This plan, by the way, extends to all employes of the company. Each year men who have accomplished some definite result, such as invention and development of a new process, or have accomplished results in any form which has brought valuable returns to the company, are awarded bonuses in the form of a certain number of shares of the common stock of the company, 5, 10, 15, 20, or more. This stock is not presented to the beneficiaries directly, but they receive the dividends on the same from the date of award. The stock is held by the company and a certain percentage is credited to it annually by a system based on the earnings of the company. By this system, the stock is paid for in a few years, when it is turned over to the recipient without restriction. If he leaves the employ of the company in the meanwhile, the amount that has been credited at that time is paid to him, but if he should die, the whole amount is paid to his heirs.

The benefits of a system of this kind are obvious. It serves as an incentive to bring out all there is in a man, and also makes him interested to remain with the company. We place great importance on this last point, that of making a man interested in remaining with the company, if he does satisfactory work. The value of a research chemist naturally increases with his accumulated knowledge. It is our policy, therefore, to continue increasing the salaries of our research chemists so that they are high enough to make a position of that nature sufficiently attractive. Too often the policy has been to make the laboratory a stepping stone to other positions to the manifest detriment of the laboratory.

The general policy of placing a comparatively large amount of responsibility on the men who do the work and having them realize that their efforts are thoroughly appreciated, and will be correspondingly rewarded if results are obtained, has contributed to make the operations of the laboratory a decided success, for it has been calculated that the laboratory has saved the company about 300 per cent of the sum expended thereon in the last three years. This amount, however, does not represent the real saving affected by the laboratory. It is based wholly on the visible direct saving brought about in the operation of a few manufac-

turing processes, where the saving on materials used, due to increased efficiency, could be directly computed in dollars and cents. The indirect gain due to improvement in product, introduction of new products, etc., has been wholly left out of this calculation. I do not think it unfair to judge of the success of a commercial research laboratory by the pecuniary saving affected thereby. No corporation is going to maintain a laboratory for any considerable length of time if it is run at a dead loss.

The ultimate criterion of the success of a commercial laboratory is whether it pays or not, and in this it differs from research work carried on for purely scientific purposes. This fact may not always be easy to determine, as the benefits are often indirect.

I have described the organization of what may be called a successful laboratory, and it will be noticed that this is carried on on a comparatively large scale; in fact, the laboratory is one of the largest in the country; while the subjects studied concern only a part of an industry which is not particularly large compared with many other industries.

I am convinced that it is useless to expect results from a small laboratory with untrained men, restricted in expenditures and apparatus, which is only too often the side from which manufacturers have approached chemical research, with the inevitable result of failure, and the conviction that chemical research is unprofitable and useless.

On the other hand, as a result of my experience with our work, it is my opinion that it would be a profitable undertaking for every large corporation in this country engaged in industries connected closely with chemical problems, to establish research laboratories on a large scale, where investigations connected with their manufacturing operations can be carried on with the assurance of all necessary funds.

The U. S. Civil Service Commission, Washington, D. C., will hold an examination on April 3-4, 1912, at various cities to secure eligibles from which to make certification to fill a vacancy in the position of assistant physical chemist in the Bureau of Mines at Pittsburgh, Pa., at a salary of from \$1,500 to \$1,800 per annum, and vacancies requiring similar qualifications as they may occur. The duties of this position will consist in conducting experiments relating to the inflammability of coal dust and mine gases. The examination will consist of the subjects mentioned below, weighted as indicated: General chemistry and physics, physical chemistry, translation into English from French or German technical works (choice of either language allowed), thesis on some subject related to physical chemistry upon which the applicant has done original investigation (to be submitted to the examiner on the first day of the examination), technical training, experience, and fitness.

APPARATUS FOR EXTRACTION WITH LIQUID NAPHTHALENE.*

By R. W. HILGENSTOCK.

The accompanying illustration shows an arrangement of apparatus for the extraction of old bones, beans, asphalt rocks, sulphur ores, etc., by means of liquid naphthalene. A short description of the process, which is protected by several patents, follows:

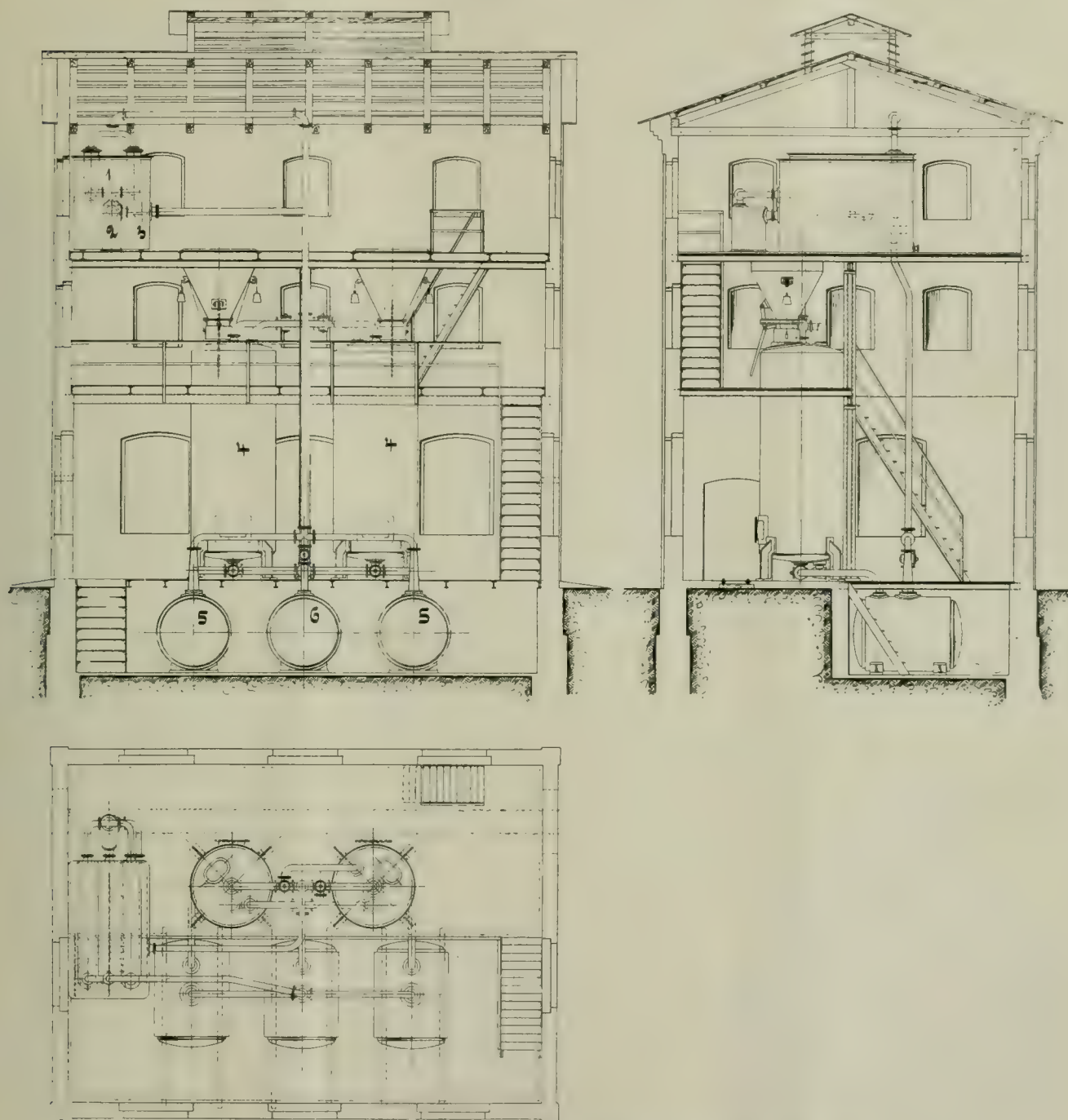
The liquid naphthalene, which leaves the storage tank, No. 3, flows through pipes which are heated in a very practical and simple manner, to the bottom of one of the extraction cylinders, constructed of wrought iron, and rises up in this vessel, thereby coming into very intimate contact with the material which is to be extracted. On top of the vessel an outlet is arranged, which is connected with another heated pipe, leading to the bottom of the second extraction vessel, No. 4, in which it is rising and coming in contact with the extraction material again. The liquid naphthalene is thereby very heavily enriched with fat, oil or sulphur, according to the raw material, and is brought continuously into one of the stills, No. 5, until the vessel is filled up; after this the second still, No. 5, takes up the enriched liquid. In the meantime live steam is led into the first still, No. 5, and the escaping steam vapors, which carry with them the naphthalene, are brought into cooler No. 1, which is kept warm enough so that the steam vapors only can condense, and the naphthalene is kept in liquid form and cannot crystallize. The mixture of liquid naphthalene and condensed steam is separated in the Florentine flask, No. 2, the liquid naphthalene flowing back to the storage tank, No. 3, while the condensed water goes to the sewer. The charging and unloading of the extraction vessels is done in the usual way; on top as well as on the bottom a large manhole is provided, through which the material can be filled in or taken out respectively. The connecting pipes between the two extractors are arranged so that the two vessels can be used reciprocally, and the naphthalene is gradually enriched on its way; the arrangement also provides that the most enriched liquid comes finally in contact with the latest charged material. Vessel No. 6 is a reserve storage tank.

The long known peculiarity of the naphthalene to volatilize very easily with steam vapors offers, in using it as extraction means, besides the great advantage of applying temperatures from 84° Cals. (its melting point) to 218° Cals. (boiling point), the further great advantage that the naphthalene can be driven off again with comparatively low temperatures from the extracted material. It is further not necessary to use tight and closed vessels provided with large coolers. A further great advantage lies in the possibility to extract with high temperatures, so that great quantities of solubles are taken out from the raw material. The process can be applied with great advantage also for the extraction of bitumen, as, for instance, asphalt

sand or mineral wax, instead of using benzol or benzine. In applying, for instance, 90° Benzol, 19 per cent of bitumen with the softening point, 70° Cals. were recovered, while with liquid naphthalene in considerably less time 23 per cent bitumen with the softening point 81° Cals. were extracted from the same material.

that escaping gases from untight tanks or vessels might ignite and cause heavy damages.

At least the cost of operation may be considered; while the steam coal consumption may not vary very much when benzine, benzol or naphthalene is applied, the price of the materials, however, is very much dif-



General Arrangement of Apparatus for Extraction With Liquid Naphthalene.

The process is very advantageous when the material which is to be extracted is mixed with about one-half of its weight with naphthalene and afterwards extracted by heating up the mixture; impure naphthalene may be used, which, in testing it with live steam vapors, is recovered as pure naphthalene. Another great advantage lies in the fact that no loss of naphthalene can occur, and furthermore in the almost eliminated danger

ferent. Benzine, for instance, sells Mks. 25 per per cent kg. today, but naphthalene can be bought for Mks. 13 per per cent kg. Considering that the loss of benzine per per cent kg. of extracted materials is about 7 or 8 per cent, while that of naphthalene for the same amount hardly reaches 1 per cent, one can very easily figure out what can be saved in using naphthalene in his extraction plant.

PURIFICATION OF LIQUID TANNERY WASTE BY FORCED OXIDATION.*

By E. C. ALSOP.

A study during a number of years of the many phases of sewage disposal leads the writer to the opinion that the whole subject of such disposal may be classed under two heads, artificial and natural.

Natural disposal would include such processes as dilution, in which the waste matter is run into water, being purified by the double action of aerobic bacteria and of direct oxidation; broad irrigation, in which the waste is spread over the surface of the ground, plowed under, and consumed by plant growth; and filtration, in which the waste is clarified and to some extent purified, by mechanical adhesion to particles of sand and by the action of anaerobic bacteria.

Artificial disposal would include chemical processes, which, however, are generally not much more than precipitating actions; septic tank processes, which are concentrated anaerobic effects; and direct oxidation by forced air blasts, use of oxygen, etc., which are nothing more than means of hurrying the natural course of events.

It would seem further that, excepting the mechanical processes in filtration and chemical precipitation, all the various processes above referred to and others may be again divided into two classes—the action of bacteria and the action of oxygen. Indeed, it is perhaps a question if in the last analysis oxidation does not fully cover the matter, as perhaps the action of the various bacteria is nothing more or less than the bringing into intimate contact with the molecule of matter affected a tiny particle of oxygen carried by the bacterium.

For centuries the trend of development in the purification of liquid wastes has been toward those means of disposal classified above as natural, starting with the simple running off of the waste into a stream, and later on to disposal farms. Artificial disposal is of quite recent use, and all its means with few exceptions are for the forced use of bacteria.

The result is poor in the extreme. The problem of pollution of streams and contamination of domestic water supply, with resultant disease and death, has been far from reaching a practical solution; and the existing conditions are not what they should be in the present light of scientific knowledge.

The above preamble is written to indicate the frame of mind of the writer for some years, and as an introduction to the remarks pertinent to the occasion. The result of this line of thought was to turn his attention to the means of purification most neglected heretofore, the use of oxygen, and to many experiments to determine whether or not the direct contact of oxygen with wastes to be purified would give a solution of this immense problem.

The late Col. George E. Waring, in the writer's opin-

ion the foremost American sanitary engineer, started a line of experiments in the same general direction and was particularly successful in them; but his heroic death cut short a remarkable career. It is to Col. Waring that any good resulting from this present work is due, as he was the inspiring spirit.

In 1905 the writer designed and built in San Diego, California, a septic tank with a vertical drop for the effluent, and with utilization of the heat of the sun by which a current of fresh air was kept passing through the sprayed effluent. The result was a clear odorless liquid, which runs in the open gutter of a city street for a mile or more without nuisance. The reason for the lack of odor in this case is the destruction by oxidation of the animal and vegetable matter remaining in the water, after the action of the anaerobic bacteria in the tank is finished. Col. Waring erected several purification plants consisting of coke filters through which air blasts are forced; and in some of these, where conditions and proportions are correct (as at Willow Grove Park, near Philadelphia) the effluent is free from objection, and for the same reason, viz., the oxidation of the matter.

These results and many others of the same nature convinced the writer that he was on the right track, and he reached the general conclusion that *if oxygen is brought into intimate contact with animal or vegetable materials in a liquid state, or a very finely divided condition in suspension in water the result is the destruction of the material into gases with a small mineral residue*; and he endeavored to conduct experiments to prove the truth of this conclusion.

Until about a year ago the writer had no particular idea of applying this system to refuse from tanneries; but a visit to the chemist of one of the large tanning companies of Pennsylvania started the thought that if the conclusions stated above were correct, the evils of the present methods of tannery waste disposal could be terminated. In pursuance of this thought, barrels of liquid waste were sent from two tanneries of a sole leather company and from a tannery of a company making upper leather, to a concern engaged in the manufacture of apparatus for the generation of ozone, and experiments were conducted for six months or more. The line of experimentation was, first, to demonstrate that all organic matter would be consumed by oxygen, and, second, to determine whether or not the system could be made commercially practicable as applied to the purification of tannery wastes.

The use of ozone in these experiments was determined on after considerable thought as not only the most efficient means of applying oxygen to the wastes on account of the extreme chemical activity of ozone but also because it appeared to be the cheapest method of securing the action of the oxygen.

The result of these experiments is that it has been scientifically proved that ozone in the proper amount will destroy all material of animal or vegetable nature with which it comes into intimate contact, and that the

*Paper presented at the Convention of the American Leather Chemists' Association, Washington, D. C., Dec. 7, 1911.

cost of operation is economical from a commercial point of view.

The essentials in a successful purification plant of the nature indicated by this line of experiments are a separation of solids and liquids, and the mechanical apparatus necessary to bring about an absolute contact between each molecule of liquid and ozone in the correct quantity.

To secure the separation of the solids from the liquids either precipitation tanks, settling basins or centrifugal separators may be used. The best plan is the use of continuous centrifugal separators, which gives perfect control of odors, and by which the solids can be placed in receptacles for incineration, for chemical treatment to recover ammonia, greases, etc., or for drying for use as fertilizers. It was not considered a part of the purification plan to determine a value for the solids, that coming directly under the scope of the tannery chemist's work.

The liquid waste, after the solids have been removed, is run through ozone atomizers in a spray tower, falling on coke filters through which currents of ozone-charged air are continually passing, as it has been found that the action of the ozone causes a slight precipitation. The coke must be occasionally replaced, but the used coke can be burned with small loss.

The effluent resulting from this treatment is entirely unobjectionable from a sanitary standpoint, and is to all intents and purposes odorless and pure. Fish placed in it live longer than in ordinary hydrant water, and it is so nearly colorless that its presence in a pure mountain stream could not be noticed at the place where it was discharged.

While the odor and appearance of the effluent are essential to the layman, they are inferior in importance, to the sanitary engineer or to boards of health, to the bacteria content. Many cultures from the purified effluent give the maximum of bacteria per cc. as 22, while many examinations fail to show even one living organism. A general average of the work shows a percentage of reduction in the number of bacteria in the raw waste to the number in the purified effluent of 99.99999; that is, one bacterium remains from each ten million present in the raw waste. In no case was any pathological bacterium found.

The general results of the experiments are then that the wastes from three different tanneries have been treated by this system and have been rendered odorless, colorless and bacterially harmless.

But while these results are important, the commercial side of the question has been kept steadily in view, and accurate accounts of consumption of electric current and of other expenses have been kept. The result is the satisfactory solution of the second aim of the experiments, and it can be set down as a safe outside figure that the cost of the treatment will in no case exceed, with all expenses of every kind, 10 cents per one thousand gallons of effluent. It is probable that the gentlemen of this association will be able

to save from the solid residue more than enough to pay all operating costs.

The cost of installation, on account of the delicate mechanism of the ozone-producing electrical apparatus and the extreme nicety of the continuous centrifugal separator, may be higher than at first would be thought necessary, but it should be in no way prohibitory; and the results should be so nearly perfect as to justify first class installation.

It is the opinion of the writer that a solution of the tannery waste problem has been found which is commercially economical and scientifically correct.

HYDRAULIC EQUIVALENT.

The United States Geological Survey prints in many of its Water-Supply Papers a list of convenient equivalents for use in hydraulic computations. The following is the most useful portion of the list:

1 second-foot equals 40 California miner's inches (law of March 23, 1911):

1 second-foot equals 38.4 Colorado miner's inches.

1 second-foot equals 40 Arizona miner's inches.

1 second-foot equals 7.48 United States gallons per second; equals 448.8 gallons per minute; equals 646.272 gallons for one day.

1 second-foot equals about 1 acre-inch per hour.

1 second-foot for one day covers 1 square mile 0.03719 inch deep.

1 second-foot for one day equals 1.983 acre-foot.

1 second-foot for one 28-day month equals 55.54 acre-foot.

1 second-foot for one 29-day month equals 57.52 acre-foot.

1 second-foot for one 30-day month equals 59.50 acre-foot.

1 second-foot for one 31-day month equals 61.49 acre-foot.

100 California miner's inches equals 18.7 United States gallons per second.

100 California miner's inches for one day equals 4.96 acre-foot.

100 Colorado miner's inches equals 2.60 second-feet.

100 Colorado miner's inches equals 19.5 United States gallons per second.

100 Colorado miner's inches for one day equals 5.17 acre-foot.

1,000,000 United States gallons per day equals 1.55 second-feet.

1,000,000 United States gallons equals 3.07 acre-foot.

1,000,000 cubic feet equals 22.95 acre-foot.

1 acre-foot equals 325,850 gallons.

1 cubic foot equals 7.48 gallons.

1 cubic foot of water weighs 62.5 pounds.

1 horsepower equals 1 second-foot falling 8.80 feet.

To calculate water power quickly:

Sec. ft. $\times$ fall in feet

————— = net horsepower on water wheel

11

realizing 80 per cent of theoretical power.

METALLURGY

WHITE IRON INSIDE OF GREY IRON.

B. B. FREUD, W. H. WIARD and J. C. HOEHN.

The phenomenon of white iron inside of grey or soft iron has been known for some time. But no adequate explanation, or even detailed description of the phenomenon, has appeared in the literature, so far as we have been able to find. This condition of "inside chill" as it has been named, is very rare and mysterious.¹ Specimens are not easily obtainable, which may account for the fact that the phenomenon has not received much attention. Mr. T. D. West² has called for specimens, so that he could study the condition, but no report has yet appeared from this source. The authors have sent a private communication to Mr. West embodying the outline of this explanation.

Mr. W. H. Wiard, chemist of the Chicago Hardware Foundry Co., has reported to Mr. West and to the authors two excellent examples of this peculiarity of cast iron.

This phenomenon has occurred only once in nine months, and but twice in two years, in the experience of Mr. Wiard at his foundry. The particular occasion in which this phenomenon developed is described in detail, so that there will be a complete description of the conditions, so far as are known, that tend to produce these specimens.

Only two kinds of castings were found faulty out of a heat of eighteen tons of castings of a similar nature. The iron was melted and run continuously in a 48-in. diameter Truesdale cupola, with Milwaukee Solvay coke, the charge consisting of:

900 lbs. of sprues,
1,300 lbs. of Peerless iron.
500 lbs. of Warner iron.

ANALYSIS OF THE IRON.

	Si.	Mn.	G.C.	C.C.	P.	S.
Peerless	3.04	.67	3.14	.24	.362	.024
Warner	4.52	.26	2.75	.13	1.850	.022

ANALYSIS OF TEST BAR.

2.96	.47	3.21	.17	.880	.055
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Commencing with the third charge, 25 lbs. of limestone was used on each succeeding charge, which numbered ten in all. The mold was made of green sand, and the iron was melted hot. An analysis of the grey iron of the casting in question gave:

Si.	Mn.	C.C.	P.
3.45	.29	.16	1.185

This analysis might indicate from the high silicon, high phosphorus, and low manganese, an improper mixing of the iron in the cupola. However, we think

this was not the case, and that the explanation must be based on some other cause.

Drawings of the castings, Figs. 1 and 2 indicate their size and in the case of Fig. 2, the extent of the inside chill. Number one is drawn to so small a scale that the extent of the chill cannot be indicated. This extended throughout the entire castings and the demarca-

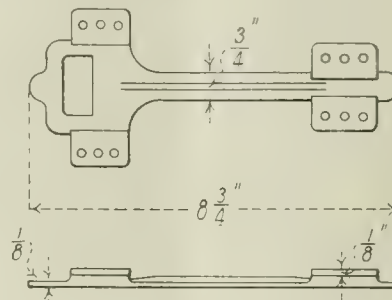


Fig. 1.

tion from the soft to the hard iron was very sharp and distinct.

It occurred to the authors that we were here dealing with a solution which could crystallize out on cooling in several ways, depending on the local conditions prevailing at the moment of crystallization. And that the phenomenon could be satisfactorily explained on the basis of the Phase Rule. Of course the phenomenon being so exceedingly rare, unusual conditions must bring it about. The authors are unable to find chemical equilibrium curves of iron, carbon and silicon alloys. But the curves of H. W. B. Roozeboom (Fig. 3) for carbon and iron will serve the purpose of this

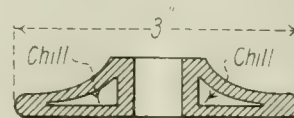


Fig. 2.

outline. We know, of course, that the presence of silicon moves the triple points considerable to the left, thus bringing the proposed explanation well within the bounds of plausibility.

By reference to these curves the explanation can readily be followed. Let us assume that there is 5 per cent total carbon present, and that the iron is poured rather cold. The outer portion immediately freezes so that no more chemical action can take place. This occurs between B and D or else between B and C. Much graphite has separated out here and so is removed from the sphere of the reaction. The casting is so exceedingly thin that the inner metal does not contain enough heat to keep the outer portion hot enough to have the chemical action between the carbon and the

¹T. D. West, Met. & Chem. Eng., Vol. IX, 6, 313.

²Foundry, Nov., 1910.

³These analyses are the records of the foundry for the time this phenomenon was supposed to have occurred. Unfortunately the exact data were not obtained. But the heats are uniform.

iron continue to the martensite and cementite area. The inner portion is more slowly cooled, and crystallizes between C and E, or even a little below E.

Thus the outer portion of the casting contains much graphite and perhaps a little martensite and is quite soft. The inner portion contains the harder compounds of iron and carbon and is therefore relatively harder.

It will be seen that this explanation assumes nothing that is not in accord with the actual foundry conditions that obtained in the case of the two instances described

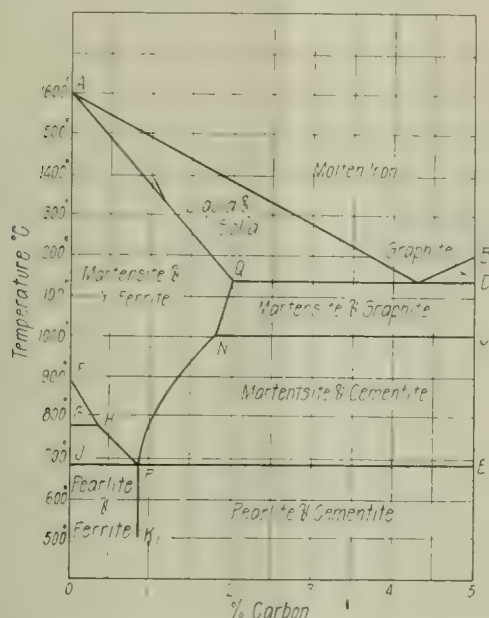


Fig. 3—Chemical Equilibrium Curves of Iron and Carbon.

here. And it is based on an equilibrium consideration that is very well established and quite generally applied. It is proposed, however, with the idea that it will provoke discussion that will lead finally to a solution of the interesting phenomenon.

We propose to test this explanation experimentally both by analysis of drillings made from various parts of the casting, and by photo-micrographical studies of etched cross sections, as soon as we are able again to produce a casting that will illustrate this phenomenon.

Arthur D. Little, in his official report as chemist of the American Pulp and Paper Association, says it has been found that certain species of bamboo are easily reduced by the sulphite process, and yield a pulp of such good color that it is at once usable for half-bleached paper. The results already obtained at the Indian Forest Research Institute are so promising that the subject will be exhaustively investigated. Referring to the work of the Philippine Bureau of Science, in the same direction, Mr. Little quotes Richmond as preferring the soda process of reducing bamboo. The yield by this process is 45 per cent, and the cost of pulp at Manila is \$21 per ton. Bamboo is considered unsuitable for mechanical pulp.

THE UTILIZATION OF BLAST FURNACE GASES.*

By EDWARD K. HAMMOND.

In smelting iron ore, according to approved practice, approximately 150,000 cu. ft. of gas is evolved from the blast furnace for every ton of pig iron that is produced. This gas was formerly discharged from stacks at the tops of the furnaces, but the presence of 25 per cent. of carbon monoxide, a gas of high calorific value, attracted the attention of metallurgists to the possibility of utilizing it for fuel purposes. The first important step in this direction was made in burning the blast furnace gases in the preheating stoves, which will be subsequently described, where the temperature of the air blast supplied to the furnaces is raised to a temperature of about 930° F. before coming into contact with the fuel. This greatly facilitates the efficiency of operating conditions, but the supply of gas produced by a given number of furnaces was found to be far in excess of that required for preheating the blast which they use. A further possibility of progress was thus presented, and with the application of internal combustion engines as prime movers for power generation it became evident that the successful application of blast furnace gases in this direction would mean an enormous saving of fuel.

As was to be expected, in a country where the natural resources have been greatly depleted, the Germans were pioneers in the application of blast furnace gases for power generation, and it is to the researches of this race of persistent investigators that the credit for this advance in the metallurgy of iron and steel is due. But when the practicability of this method had once been demonstrated, the industrial companies of our own country acted with their characteristic initiative, and we now have several power plants operating upon blast furnace gases.

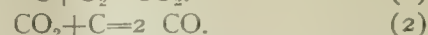
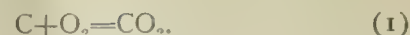
By far the most important of these is the installation at the Gary Works of the Indiana Steel Co., where the scale upon which this principle has been applied far exceeds that of any other plant in the world. It is worthy of notice in this connection that, at the time when the use of blast furnace gases was decided upon as a source of power, practically no operating experience had been obtained in this country, where differences in ore, fuel and metallurgical practice combined to render the results obtained in Europe of little value. Work had been conducted in this country upon an experimental scale and plants had been ordered for installation at the South Chicago Works of the Illinois Steel Co., for the Edgar Thomson Mills at Pittsburgh, and for the Lackawanna Steel Co. at Buffalo. The latter installation was completed and placed in operation in 1902, which gives it the credit of being the first plant of its kind in the United States. But neither of these plants

*From the *Armour Engineer*.

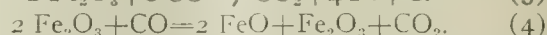
were in operation at the time that the equipment was ordered for the Gary Works, so that the courage in their convictions exhibited by the designers is particularly noticeable. Nor was this confidence misplaced, for, after two years of successful operation, it has been found that the load can be carried with the greatest regularity.

When completed, the Gary Works will have 16 blast furnaces at their command. At the present time, however, eight furnaces comprised in the groups of 5 to 12 are in operation and the system for the utilization of blast furnace gases refers to their production. Furnaces 1 to 4 are now in course of construction and a complete installation for using the gases which they produce is being built.

Before entering upon a discussion of the methods that are used to fit these furnace gases for use in the gas engines, a brief consideration of the reactions that



For the sake of simplicity, we shall assume that the ore in the furnace is a pure red hematite, which has the composition Fe_2O_3 . The following reactions will then commence as soon as the ore enters the furnace:



If these were the only reactions taking place between the ore and the fuel at the top of the furnace, the gas given off would be carbon dioxide, which has no fuel value. But reactions (3) and (4) are limited by the fact that both metallic iron and carbon have the power of reducing carbon dioxide to form combustible carbon monoxide according to the reactions shown in equations (5) and (6).

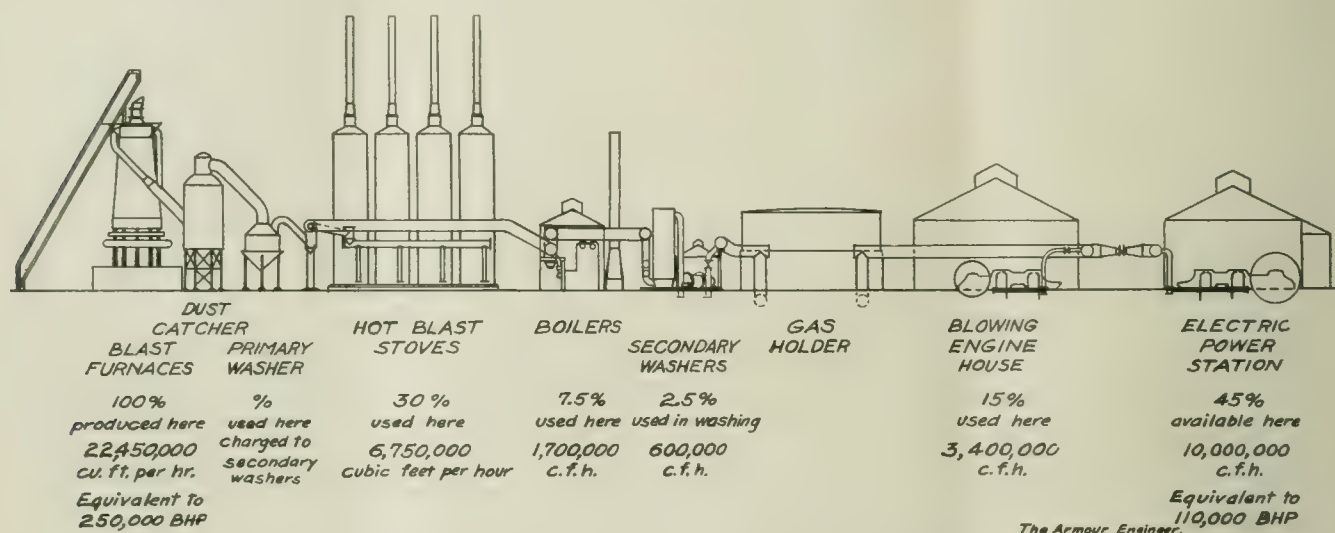


Fig. 1—Diagram Showing the Arrangement of Equipment.

are responsible for their formation will not be out of place. For the benefit of non-chemical readers, it may be mentioned that the blast furnace consists of an approximately cylindrical structure, those at Gary being 88 ft. in height by 32 ft. in diameter. These furnaces are lined with fire brick. Neglecting the fluxing material that is added to remove impurities, the charge consists of iron ore and coke which is fed into the furnace by a car that runs up the inclined track shown in Fig. 2. A bell-shaped valve at the top of the furnace admits the charge as required but prevents the gases from escaping. The pipe that surrounds the furnace at the base delivers the blast of preheated air through openings called tuyeres. The blast then rises through the bed of ore and coke in the furnace and leaves through the openings at the top, that communicate with two ducts which carry away the gas. The process by which carbon monoxide is formed is somewhat complex but may be fairly well expressed by the following equations. Upon entering the furnace, the oxygen in the blast reacts with the coke, which is at a red heat, according to the following two equations:

The result is that the gases which are evolved from the furnace have an average composition which is expressed by the analysis given below:

CO	25%	Carbon monoxide.
H	3%	Hydrogen.
CO ₂	12%	Carbon dioxide.
N	60%	Nitrogen.

and this gas has an average calorific value of 95 B.T.U. per cubic ft.

The successful use of blast furnace gases in internal combustion engines depends very largely upon the degree to which the purification has been carried. This fact has led to the installation of a most complete equipment at the Gary Works for carrying out the various purification processes through which the gas passes before it reaches the different points of consumption. A good idea of the arrangement of this equipment will be obtained from the diagram shown in Fig. 1, which presents a panoramic view of the equipment, together with data concerning the quantities of blast furnace gas used in different parts of the plant.

The gas produced in each furnace is discharged

through four openings at the top, as shown in Fig. 2, and enters two ducts called "downcomers" which carry it to the first dry cleaner or primary dust catcher, where the bulk of the dirt and ore dust is removed. These dust catchers are cylindrical tanks 45 ft. in height by 25 ft. in diameter, with conical tops and bottoms, and, like the downcomers leading to them, they are made of steel plate without any fire brick lining; the purpose is to cool the gases as far as possible by radiation from the plates. The dust-laden gases entering these catchers have their direction of travel abruptly changed, and at the same time their speed is greatly reduced, owing to the increased cross-sectional area. This results in settling out a large part of the dust. The gases leave these primary dust

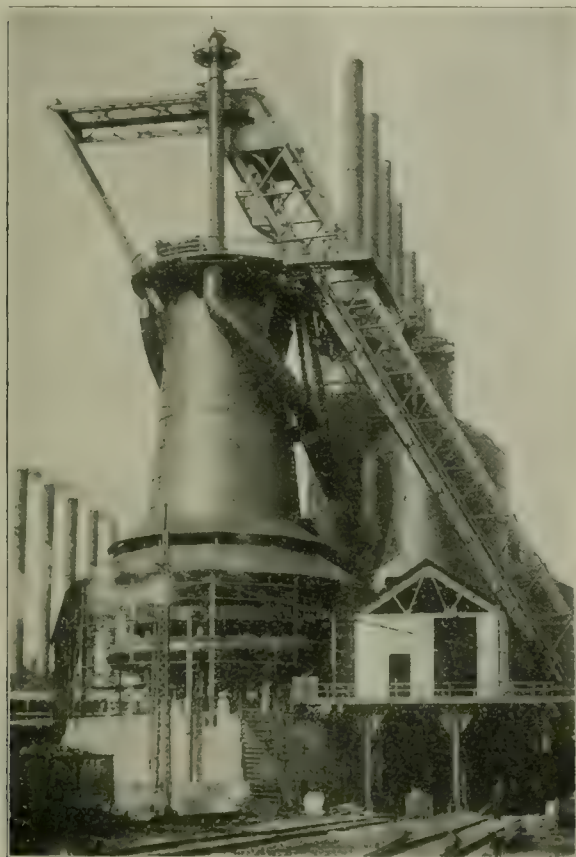


Fig. 2—Blast Furnace, Dust Catchers and Preheating Stoves.

catchers at the top and are carried to the secondary dust catchers, which are of exactly the same type but smaller, their size being 30 ft. high by $18\frac{1}{2}$ ft. in diameter. These secondary catchers remove a further part of the dust carried by the gas and also serve the purpose of water seals when it is required to shut down the furnace for repairs. This is made necessary through the arrangement of the furnaces in pairs, each furnace of the pair discharging its gases through primary and secondary dust catchers into a common main. When one of the pair of furnaces is shut down, its secondary dust catcher is filled with water to a level above the inlet pipe, thus forming a water seal that prevents the gases from the opposite furnace from backing through it.

The preceding description of gas purification applies to the two pairs of furnaces comprised in the group 9 to 12, which were the first ones to be built. The same method of preliminary purification is followed with the gases from furnaces 5 to 8, but the process is carried a step farther. In this case the gases issuing from the secondary dust catchers pass into large settling tanks which are 40 ft. in diameter by 25 ft. high, one of these tanks being provided for each pair of furnaces. In passing through these tanks, the speed of the gas is so far reduced that a further portion of the dust with which it is contaminated is allowed to settle out. These settling tanks discharge the gas passing through them into a common main, which corresponds to the one uniting the secondary dust catchers of furnaces 9 to 12. All of the dust catchers are equipped with bell bottoms through which the dirt which they collect is discharged into cars that run on tracks passing under them.

In all cases the gases now pass to the groups of primary washers, three of which are provided for each pair of furnaces. Each of these washers has a capacity sufficient to take care of the gases produced by a single furnace, so that one of the group is always available in case it is necessary to shut down a washer for repairs or cleaning. Fig. 3 illustrates one of these washers in course of construction, showing that they are cylindrical in shape, with conical tops and bottoms. These washers are 40 ft. in height by 22 ft. in diameter, and they are filled about one-third full of water, this level being maintained constant by overflows. Fresh water is fed in from pipes at the top. The gas is led into these washers at the top and carried down almost to the surface of the water by means of a central pipe, which is provided with a fluted mouth to spread the gas out over the greatest possible surface. In this way a considerable amount of the dust still carried by the gas is thrown down and absorbed by the water. After impinging upon the water, the gas rises to the top of the washer and leaves through two openings, one at either side, where it passes through dust legs into the main. At this point a division of the gas is made, according to the data presented in Fig. 1. The gas that is to be used for preheating the blast in the stoves and for use under the boilers has been sufficiently purified, and the required amount is diverted for these purposes.

Eight preheating stoves are used in connection with each pair of blast furnaces, as shown in Figs. 2 and 3—four stoves for each furnace. These stoves have a central flue surrounded by a checker work of fire brick, and in operation the gas, mixed with the necessary amount of air for its combustion, is burnt in the central flue. The hot products of combustion then pass down from the top of the flue through the checker work and then out into the stack. This results in heating up the checker work to a bright red heat. In using the stove for preheating the air blast the process is reversed. In this case the air passes up through the

hot checker work, where its temperature is raised to about 930° F., and then down through the central flue and out into the duct leading to the furnace. The stoves are used in rotation, each one being heated up for a period of one hour, after which the valves are reversed to shut off the gas and admit the air blast.

the plant to obtain a gas supply for the blowing engines which depend upon this fuel. The boilers also supply the two General Electric Curtis turbines in the electric power station, the hydraulic presses used in the plant, and small amounts of steam for other purposes. The boiler equipment consists of sixteen

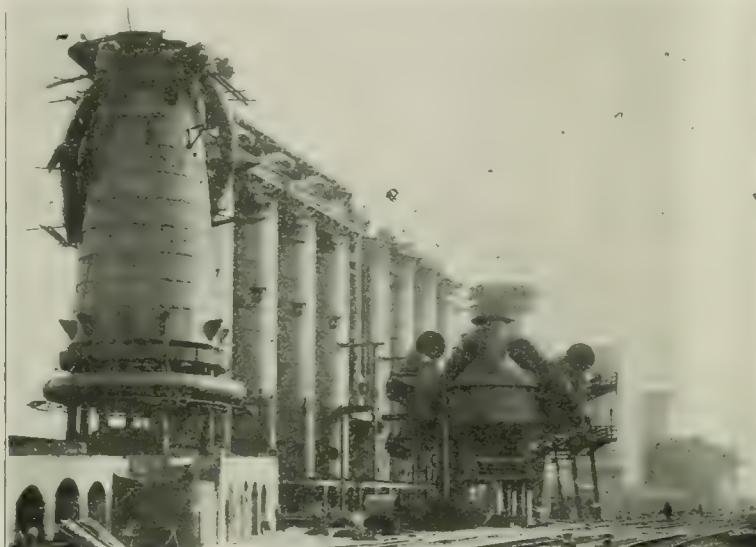


Fig. 3—Primary Washers, Blast Furnace and Preheating Stoves in Course of Construction.

As shown in the diagram, 30 per cent of the gas from the furnaces is used in the preheating stoves, this amounting to 6,750,000 cu. ft. of gas per hour.

The boiler settings, where the blast furnace gases are used for fuel, have been modified so that they may be used for either gas or coal. When the plant

units of 400 hp., which thus provide a reserve of 6,400 hp. The boilers are of the Sterling and the Rust water-tube types, eight boilers of each kind being housed in separate buildings. A firing bed of coal is maintained under the boilers, which is hand fired on account of the small amount of fuel that is used. It

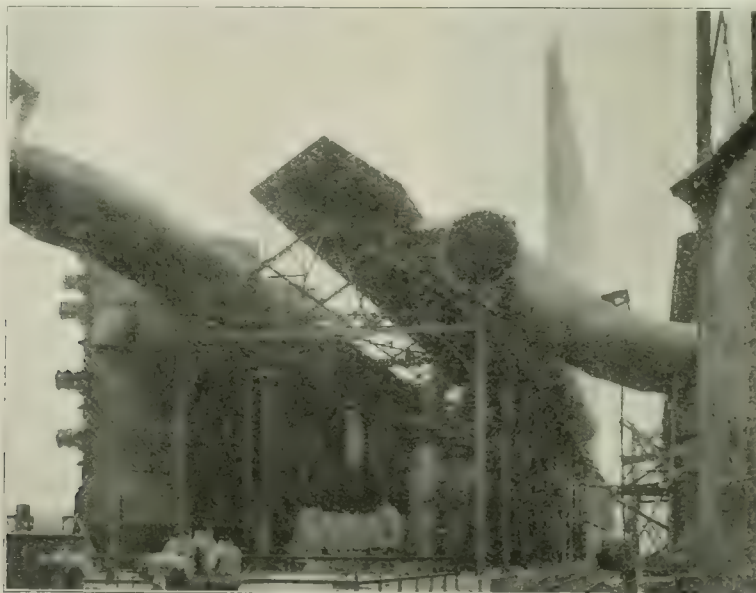


Fig. 4—General View of Secondary Washers, Water Separators and Gas Holders.

is operating under normal conditions the boilers are of relatively small importance, only enough steam being maintained to keep the four steam blowing units going, the idea being to have them available for taking up the load in case of the failure of the gas engines. These steam blowers are also necessary in starting up

will be seen in the diagram that $7\frac{1}{2}$ per cent of the total gas supply, or 1,700,000 cu. ft. of gas per hour, is burned under the boilers.

Returning to the portion of the gas requiring further purification to fit it for use in the gas engines, it will be seen in the diagram that a duct conveys it

from the primary to the secondary washers. This duct is provided with a series of dust pockets which assist in removing some solid impurities from the gas passing through them. Four Zschocke washers are used to treat the gases from each pair of furnaces and each of them has a Theisen washer connected in series with it. The design of the Zschocke washers used at Gary has been modified in that they have the checker work placed above the baffle plates in a single vertical drum 60 ft. in height. These washers will be seen at the extreme left in Fig. 4. The building which houses the Theisen washers is shown in course of construction in this picture, where one of the washers is plainly visible. The water separators, which will be subsequently mentioned, are the vertical cylinders to the right of the Theisen washers from which the gas passes into the main leading to the holders, shown at the extreme right.

water, which takes up any impurities which are still held in suspension.

The gas is now free from all impurities except a considerable amount of moisture that has been taken up in the washing processes and is carried in the form of mist. This moisture is removed in the water separators, shown at the right of the Theisen washers in Fig. 4, which consist essentially of boxes containing iron shavings. The gas strikes these shavings at high speed and deposits most of the water which it carries upon them. It then reverses its direction of travel, so that there is no opportunity for the water to be picked up again. Passing on from the water separators, in a comparatively dry condition, the gas goes into the holders under a slight pressure. These gas holders are 90 ft. in diameter and 30 ft. in height and are of the standard type.

Reference to the data presented in Fig. 1 will show



Fig. 5—Interior View of Blowing Engine House.

The gas enters at the base of the Zschocke washers and traverses a winding course between the baffle plates in the lower half of the drum. On leaving this section the gas rises through the checker work, where it meets a spray of water from the top. This water is fed into the washer through Schutte & Koerting spray nozzles which are mounted on radial pipes extending out from a central water main, the purpose being to obtain the greatest possible distribution. This treatment removes the greater part of the dust which is still carried by the gas. On leaving the Zschocke washers it enters a building which houses the Theisen washers, where the final step in the purification process is carried out.

The Theisen washer consists of a steel cylinder which surrounds a revolving drum that carries a number of vanes on its periphery. This drum is driven at 350 r.p.m., and the vanes pick up water at the bottom of the cylinder and spread it over the entire inside surface of the machine. As the gas passes through these washers it impinges upon this film of

that 15 per cent of the total gas supply, amounting to 3,400,000 cu. ft. per hour, is used in the gas engines that drive the blowers. These engines are housed in two buildings, one of which supplies each group of four blast furnaces through independent blast mains, but a common gas main connects the two stations to provide for a possible failure in the gas supply from one group of furnaces. Fig. 5 shows an interior view in one of these stations, the equipment of which consists of eight gas blowing units, having a total capacity of 265,000 cu. ft. of free air per minute, and two steam blowing units, having a capacity of 45,000 cu. ft. of free air per minute. The steam units are held entirely in reserve, and three gas units and one reserve are operated to supply each pair of furnaces. Each gas-driven blower has a capacity of 33,000 cu. ft. of free air per minute. The division of output will thus be evident.

The gas engines have a rated capacity of 3,000 indicated hp., and the steam engines 3,500 indicated hp.

The general arrangement of the equipment is essen-

tially the same as that of the electric power station, which will be subsequently described. The results obtained in operating these gas engines to supply blast to five furnaces are presented in Table I.

An interior view of the electric power station is shown in Fig. 6, which gives a good idea of the general arrangement of the equipment. There are seventeen twin-tandem, double-acting gas engines running at $83\frac{1}{3}$ r.p.m. Fifteen of these are arranged for direct coupling to 25-cycle, 3-phase, alternating current generators, which furnish power at 6,000 volts. The other two gas engines are arranged for direct coupling to 250-volt direct current generators. These twin-tandem engines have a rating of 4,000 hp., and the generators of 2,000 kilowatts, but in order to assure having ample power they are designed to carry a 30 per cent overload. Two General Electric Curtis turbines, of 2,000 kilowatts capacity, have also been installed in this station for use in case of emergency.



Fig. 6—Interior View of Electric Power Station.

The twin-tandem engines were built by the Allis-Chalmers Co. and do not differ materially from their

TABLE I.—DATA ON OPERATION OF GAS BLOWING ENGINES FOR MONTH OF OCTOBER, 1911. FURNACES 5, 6, 7, 8 AND 11.

	Av. i. h. p. developed.	Av. total cu. ft. gas per day.	Av. cu. ft. gas pr. i. h. p. hr.	Coal eq. gas pr. i. h. p. hr.
5.....	2,663	8,924,000	139	1.32
6.....	2,885	9,669,000	140	1.33
7.....	3,007	10,066,000	139	1.32
8.....	2,819	9,420,000	139	1.32
11.....	2,704	9,300,000	143	1.36

14,078

14,078.8=1,760 average horsepower per engine.

Cubic feet of gas given is equivalent cubic feet at 100 B. t. u.

Average B. t. u. of gas for October, 1911, was 94.5.

standard engines of that type. As shown in the illustration, they are set crosswise of the building, where the cylinders are conveniently situated for connection with the fuel supply. The gas mains for this purpose pass over from the holders at a sufficient height to clear the tracks and connect with a main running along the wall of the electric power station. The leads to

TABLE 2.—COAL SAVED THROUGH USING BLAST FURNACE GASES AT THE GARY WORKS.

Total capacity of gas engines installed to date:

	Horsepower.
17 engines at 2,500 K. W. or 3,350 H. P.....	56,950
16 engines at 2,000 H. P.....	32,000
6 engines at 3,000 K. W. or 4,000 H. P.....	24,000

112,950

Or say 113,000

Running 24 hours per day and 30 days a month, the total horsepower hours in one month would equal—

113,000x24x30, or 81,360,000 H. P. hours.

Taking average cubic feet of gas per I. H. P. at 130 and coal equivalent per I. H. P. at 1.3, the total coal equivalent would be—

81,360,000x1.3:2,240, or 47,000 gross tons (about).

Taking efficiency of steam engine at 10 per cent and gas engine at 25 per cent, the saving in coal by using above capacity in gas engines over steam engines would be 70,500 gross tons per month.

the engines enter the building at the level of this main and then drop down below the floor level, as shown in Fig. 6, where the connections with the engine cylinders are located. The exhaust from the engines is de-

livered into a tunnel running parallel with the power station. This tunnel communicates with a steel stack 92 ft. in height, which carries away all objectionable vapors given off and also does away with any nuisance from the noise of the engines. It will be seen, in the data presented in Fig. 1, that 45 per cent of the total gas supply, amounting to 10,000,000 cu. ft. per hour, is used in the gas engines in this power station.

The saving effected through the use of blast furnace gases in generating power will be evident from the fact that, for every ton of pig iron produced per day, 25 brake hp. is available for power purposes, outside of the power required to operate the blast furnaces, provided this power is generated in gas engines.

An idea of the magnitude in the saving for coal at the Gary Works, through the use of blast furnace gases for the engines in the electric power station and the blowing engine houses, may be obtained through reference to Table 2. The importance of this station from an economic standpoint will be further appreci-

ated when it is known that all of the electric power used in the Gary mills is but a fraction of the output of the electric power station. The City of Gary obtains all of its electric power from this source, the current being sent out at 6,600 volts and transformed to the desired voltage. In addition to this, The American Bridge Co., The American Sheet & Tin Plate Co. and The Buffington Cement Works obtain all of their electric power over a 22,000-volt line from Gary. And all of this power is obtained through the utilization of a by-product—a source of revenue which most of the steel mills in this country allow to go to waste..

A recent U. S. Consular report gives the following figures regarding the Swedish Iron Industry: The plants in operation at the close of 1911, in comparison with previous years were as follows:

	1909.	1910.	1911.
Blast furnaces	66	97	96
Hearths	186	217	212
Bessemer plants	15	17	18
Martin plants	46	53	52

The production in the principal lines for the last 10 years has been as follows:

Year.	Pig iron. Tons.	Blooms. Tons.	Bessemer ingots. Tons.	Martin ingots. Tons.
1902.....	538,100	186,100	84,000	196,000
1903.....	506,800	192,300	84,200	227,100
1905.....	528,500	189,200	78,600	245,400
1905.....	539,400	182,600	78,200	281,500
1906.....	604,800	178,300	84,600	302,400
1907.....	615,800	174,400	79,000	333,000
1908.....	567,800	152,300	81,100	347,900
1909.....	448,000	120,700	63,300	248,800
1910.....	604,300	150,500	97,900	370,700
1911.....	633,800	146,700	93,800	364,400

Swedish exports of iron and steel (not ore) for the past two calendar years were as follows:

Articles.	1910. Tons.	1911. Tons.
Pig iron	134,100	150,500
Scrap	9,400	7,900
Ingots	13,500	11,200
Blooms and rough bars.....	31,400	27,600
Billets and massive tube blks.....	25,500	28,600
Bar iron	141,200	129,200
Bar ends	6,100	6,400
Wire rods	33,400	33,700
Plates	2,400	2,200
Pipe and fittings.....	14,300	10,700
Wire, drawn	2,900	3,000
Nails and horse nails.....	7,100	7,300
Total	421,300	418,300

The municipality of Amsterdam has announced an international gas exhibition in that city, to be opened Sept. 14 next and closed Oct. 6, with a possible extension of a week's duration. The exhibition will be held in the Industrial Palace, a large, many-windowed edifice, with spacious rooms and a garden. The main object is to exhibit the various appliances used for illumination and for other purposes, both domestic and industrial. It is also expected to have lectures on appropriate topics relating to gas.

SURFACE COMBUSTION.*

By RAYMOND C. BENNER.

The fundamental principle underlying surface combustion, which has been extensively studied by W. A. Bone, is that all hot surfaces accelerate chemical changes in gaseous systems. In the case of electrolytic gas enclosed in smooth glass walls, say at 450°C., a negligible amount of steam may be formed. Certainly, this may be said to be the tendency there. By placing in this vessel some porous substance, so that a much larger surface is exposed to the gas, chemical union is caused to take place at a measurable rate at the surface, not rapidly enough, however, to cause an explosion. It is therefore necessary to distinguish between two possible conditions under which gaseous combustion may occur: (1) Homogeneously—that is to say, equally throughout the system as a whole, at temperatures below the ignition point, slowly and without flame, and at temperatures above the ignition point rapidly and with flame; (2) heterogeneously, or only in layers immediately in contact with an incandescent surface. The latter is surface combustion and the process is much more rapid than is the normal combustion in ordinary flames.

The fact that metals of the platinum group aid in the chemical union of gases has long been known, but that hot surfaces in general have this acceleratory influence on gaseous combustion has, in all probability, escaped recognition of technologists because of the idea possessed by Siemens, that combustion was retarded by hot surfaces. Before Siemens' time this subject seems to have received the attention of a number of men such as Döbereiner, Davy, and others, but with no explanation of the phenomena or practical results other than Döbereiner's lamp.

The fact that all surfaces, depending on their chemical and physical properties, accelerate combustion at temperatures below the ignition point, is not the only point to be considered. Treatment in various manners can change the rate greatly. For example, if a surface consisting of a non-oxidizable metal or non-reducible oxide be exposed to H or CO before use, its action in bringing about their union with O is greatly stimulated. If previously exposed to O the rate of combustion is decreased. The relative affinities of different substances for O in ordinary combustion may be changed in the presence of hot surfaces; under ordinary conditions O has a greater affinity for CH₄ than for H or CO. This is reversed in the presence of a hot surface. H₂O is probably essential to the burning of CO under ordinary conditions, but it has been shown to greatly retard surface combustion.

Mr. Bone's experimental work leads him to believe

*From the Mining and Scientific Press.

†Chief, Boston Food and Drug Inspection Laboratory.

•Circular No. 91, U. S. Bureau of Chemistry.

‡Lac and the Lac Industries, by George Watt, reporter on Economic Production to the Government of India. The Agricultural Ledger, 1901, No. 9.

§Loc. cit.

that the accelerating power of surfaces increases with temperature; and the difference which different bodies show in the rates of acceleration tends to disappear with increase of temperature. When explosive mixtures of gases are forced through incandescent porous substances, the rate of combustion is so greatly hastened that combustion takes place within the pores at a rapid rate. Therefore the surface of the porous diaphragm is kept in a state of incandescence without flame. The two chief points here emphasized are, that the term "pore" is not used in the gross sense, but in that of molecular dimensions, and that the incandescent surface plays a truly important part in inciting chemical action.

The advantages claimed for surface combustion are: (1) Great concentration of heat in a small space, because of the greatly increased rapidity of combustion; (2) combustion takes place without excess of air, thus doing away with one great loss of heat essential to

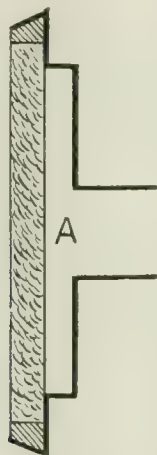


Fig. 1.

ordinary combustion operations; (3) temperatures, due to the foregoing reasons, are higher than otherwise possible without regenerative devices; (4) the large amount of radiant energy developed makes the transference of heat much more rapid. The heating diaphragm, shown in Fig. 1, is made of granules of fire brick bound together with a suitable material. This diaphragm, the structure of which is readily seen in the figure, is quite porous, so much so that $\frac{1}{8}$ -in. water pressure readily forces air through it. The air and gas are supplied to the mixing chamber "A" either by means of a Y-tube and low pressure (2 to 3 in. water) gas and air or by means of an injector, by the use of which gas can be supplied at two pounds pressure.

In starting, the gas is admitted alone and ignited, after which the air is turned on gradually. The flame becomes non-luminous and smaller in size until the correct percentage of air and gas is being used, when it disappears and only an intensely hot surface without flame remains. But a thin surface layer of the diaphragm becomes hot ($\frac{1}{8}$ to $\frac{1}{4}$ in.), while the back of the apparatus remains cool enough to touch with the hand. Unburned gases do not escape from the surface

and the temperature rises immediately upon increasing the supply of gas. Temperatures up to $850^{\circ}\text{C}.$ are easily maintained on a freely radiating surface. The diaphragm can be used equally well in any position and with any of the ordinary forms of fuel gases, the amount of heat generated depending, of course, upon



Fig. 2.

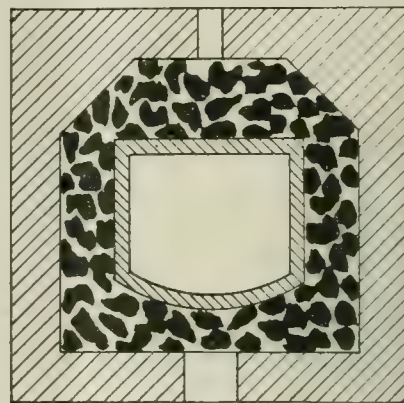


Fig. 3.

the kind of gas used. The gas surrounding the incandescent surface has no effect whatsoever upon the combustion; in an atmosphere of CO_2 the diaphragm acts as well as in air.

An interesting experiment, showing one of many applications to which this method of heating can be applied is the evaporation of sodium silicate solution by placing the diaphragm above the dish containing the solution, so that the upper layers of the solution are heated by radiant heat. As evaporation takes place the dry silicate can be skimmed off. This method is much easier and more satisfactory than trying to evaporate a solution of this nature by heating from below.

The second application of the process can be used equally well for gases and vapors. Figs. 2 and 3 make the explanation simple. The explosive mixture of air and gas is forced through an orifice in the base of either a muffle or a crucible furnace at a rate more rapid than that of back firing. The combustion takes place in the bed of granular refractory material, no flame coming out of the top of the furnace. The intensity of the temperature obtainable may almost be said to be limited only by the fusibility of the refractories. These furnaces are started in the same way as the diaphragm, but at the expense of more time. The following table shows the great efficiency of this arrangement, when it is remembered that in order to maintain a muffle of similar size and shape at $1055^{\circ}\text{C}.$, 105 cu. ft. of gas per hour is required, when the muffle is heated by the ordinary method employed in gas furnaces.

RESULTS OF TEST ON A MUFFLE FURNACE.					
(Dimensions of muffle, 9½ by 5¼ by ¾ in.)					
Temp. middle of muffle.		Gas consumption to maintain temp. constant, cu. ft. per hr.		Temp. of products.	
°C.	°F.	at 15° C.		°C.	°F.
815	1,409	21.0		540	1,004
1,004	1,840	35.3		645	1,195
1,205	2,201	58.0		870	1,598
1,424	2,596	79.0		1,085	1,985
Mean net cal. val. of gas, 540 b.t.u. per cu. ft. at 15° C.					

The application of the principles of surface combustion to steam boilers becomes of great interest, remembering that the average thermal efficiency of gas-fired boilers is not far from 65% and that nearly 95% efficiency has been obtained by the new method. The arrangement used with a small boiler of cylindrical section three feet in length traversed by tubes three inches in diameter is simple. The whole length of the tubes is packed with granular refractory material of the proper size, the front end fitted with a clay plug, containing an opening of such size that the speed of entering explosive mixture will be greater than that of back firing, each tube communicating with a mixing chamber of especial design. The products of combustion leave the boiler at not more than 70°C. above the temperature of the water in the boiler and pass through a feed-water heater, which they leave with a temperature of less than 100°C. The details of the experiment with a 10-tube boiler bring out the advantages possessed by this system:

Pressure of gas and air, 17.3 in. (water gauge).
 Steam pressure, 100 lb.
 Products of combustion leaving boiler, 230°C.
 Products of combustion leaving feed-water heater, 95°C.
 Water entering feed-water heater, 5.5°C.
 Water entering boiler, 58°C.
 996 cu. ft. of gas of 562 b.t.u. per cubic foot.
 559,800 total b.t.u. of gas.
 527,800 b.t.u. used in heating water.

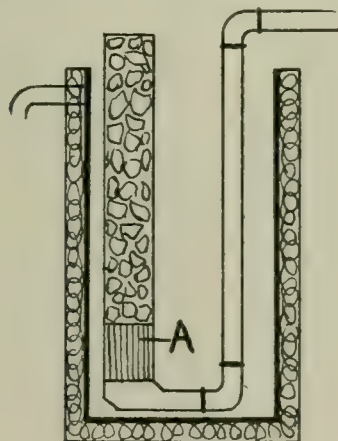


Fig. 4.

94.3% of total heat generated used in evaporating water.

The advantages of this system of combustion when applied to boilers may be briefly summarized as follows:

(1) Little if any excess of air is necessary to obtain perfect combustion; (2) with 0.5% oxygen in the products of combustion, combustion was complete; (3) steep heat gradient; (4) 70% of the evaporation occurs in the first third of the tube, 22% over the second third, and only 8% over the last third; (5) the mean evaporation is very high, over 20 lb. of water per square foot of heating surface; (6) while evaporating

20 lb. of water with an efficiency of nearly 95%, the equipment can be forced 50% higher with but little loss in efficiency.

Among the many openings for the application of this new method of heating, that of melting metal and other low-melting alloys, seems to be one of the most attractive. This is simplicity in itself and the method of operation is quite evident (Fig. 4). The explosive mixture of gas and air is forced through a clay plug (A) into a pipe fitted with several pieces of a suitable rebustion takes place in a manner entirely similar to that described for the crucible and muffle furnaces. The following table gives a good idea of the efficiency of this process when applied in this way:

LEAD-MELTING TEST.

	°C.	°F.
Temperature of metal charged.....	15	60
Temperature of metal tapped.....	372	682
Temperature of gases leaving apparatus.....	500	932

Lead melted per hour, 1176 lb.

Heat required per hour to raise metal from 15°C. to 372° (1176 by 32.57), 38,420 b.t.u.

Gas burned per hour, 100 cu. ft. at normal temperature and pressure.

Net cal. val. of gas, 559 b.t.u. per cu. ft. at normal temperature and pressure.

Ratio, 38,42 : 55.90 = 0.686.

A NEW MATERIAL FOR AMERICAN PAPER MILLS.

In his report as chemist to the American Paper and Pulp Association, Arthur D. Little of Boston has called attention to the availability for American paper mills of Algerian esparto, the fiber of Spanish grass. Mr. Little says:

Your chemist has recently received several interesting communications from Mr. John Christie, the well-known fiber expert and broker of London, urging a more general consideration of esparto by American paper makers. Although upwards of three-quarters of a million tons of chemical mechanical wood pulp are imported into the United Kingdom annually, it has not had the effect of diminishing the consumption of esparto, which stands at about 200,000 tons, which is a little above the average of the past twenty years. Nearly half of this amount comes from Algeria where great quantities remain untouched for lack of a market. It should be possible to lay down Algerian esparto in American ports at an advance of only about \$2.50 above its price in British ports. It seems therefore reasonable to believe that first quality Algerian esparto could be laid down in the United States at £4 per ton of 2,240 lbs., including freight and insurance. The experience of English paper makers has demonstrated beyond question that esparto stands in a class by itself as a raw material for the manufacture of high grade book papers, and it would seem as though it were well worth the serious consideration of paper makers in this country.

English Gas Producers and By-Product Plants.

The following description of some of the newer gas producers and by-products plants installations in Great Britain is taken from the London Times' Engineering Supplement.

Two at least of the largest steel works in Sheffield have installed plants for generating gas from which sulphate of ammonia, tar, and oil are recovered, the gas being used for steel melting, heating, and power purposes throughout the works. The first plants were supplied by a gas power and by-product company of Glasgow, and have now been in operation for a considerable period. The general principles of the method employed in such apparatus are now well known, but in recent designs important improvements have been incorporated.

Examples of the newer types of plant are now being installed. The latest form of producer is fitted with a rotating top and mechanical stokers, which not only permit the use of coking and inferior fuels, but with ordinary fuels have been shown to increase the rate of gasification by 50 per cent. Hand stoking is entirely eliminated, and it is claimed that higher yields of sulphate of ammonia are obtained, with at the same time richer gas. The fuel is tipped from the wagons into a hopper pit, and from there is elevated and conveyed mechanically to hoppers which are placed over each producer.

In the older type of producer 1 fireman could feed efficiently into the producer about 2 tons 10 hundred-weight of fuel an hour, whereas with the newer type 1 man can deal with 6 tons of fuel an hour. The gases leaving the producer pass through a superheater of special design (so arranged that the hot gas is utilized in preheating the air and steam in the blast on its way to the producer grate), and subsequently pass through a mechanical washer where all dust is removed and a suitable gas temperature obtained for the recovery of sulphate of ammonia.

This latter operation is performed in a lead-lined tower, the gas being washed with ammoniacal liquor containing a small percentage of free sulphuric acid. After leaving the acid tower, the gas is treated either in gas-cooling towers or in washers of special design, so that it is rendered comparatively free from moisture. Owing to the complete gas-cooling arrangements which have been incorporated in the later designs, the furnace efficiency of the gas has been considerably increased. The hot water from the first of these cooling towers is used for saturating the blast for the producers in a specially constructed tower, a process leading to further economics, as the greater part of the steam necessary for the producer blast can be obtained in this manner.

The tar recovered is run into collecting vessels, from which it is blown into railway-tank wagons or storage tanks. There is considerable value in the pitch and creosote oil obtained from this tar. The sulphate liquor

obtained in the acid tower is evaporated in a vacuum pan, fitted with an automatic discharger, so that the sulphate is discharged continuously into a centrifugal drier, after which it is ready for dispatch. It is stated that from 85 to 100 pounds of sulphate of ammonia can be obtained per ton of fuel gasified without in any way affecting the suitability of the gas for general use in steel works. Taking the net value of the sulphate recovered at £10 (\$48.65) per ton, the present price being £14 (\$68.13) per ton, a credit should be obtained of 8s. (\$1.95) per ton of fuel gasified.

It is claimed that the repairs to the furnace are considerably less with the washed gas, especially in regard to the gas and air reversing valves and the checker chambers. It is well known that with ordinary producer gas coming hot from the producer considerable trouble is experienced with the warping of the valves, and as the washed gas is from 200° to 300° C. cooler at the furnace, and the exit gases are also cooler in approximately the same ratio, the life of the valves is considerably increased. It is also found that with a suitable design of furnace the renewal of the checker work is greatly reduced.

While the use of acetic acid in the Far East in the coagulation of latex is almost universal, there being few instances in which sulphuric acid is used, the formic acid prepared by the Factory of Chemical Products, Scheidam, Holland, according to Greiner's Rubber News, has solved the problem of the best and cheapest coagulating agent. It is stated that not only is the formic acid the cheapest of the organic acids, but it is more powerful in its action than any other compounds of the class. The makers claim that they are in a position to offer a grade containing 90 per cent of free acid, with specific gravity 1.20, 46 parts of which are theoretically equal to 60 of acetic acid, 63 of oxalic acid, 70 of citric acid, and 75 of tartaric acid. It is described as an effective and antiseptic coagulating agent, without any harmful effect upon the rubber and preventing agglutination. Interest attaches to the statement that the tests of Spence prove that the rubber obtained by a treatment with formic acid is as good if not better than the product obtained by the use of acetic acid.

According to imperial statistics, the total value of Germany's exportations of "glass apparatus and instruments for industrial or scientific purposes" was \$1,939,462 in 1911 and \$1,627,444 in 1910, the shipments to the United States amounting to \$362,959 and \$339,579, respectively.

The manufacture of leather in Japan has been steadily declining since 1904, when the output was valued at over \$9,000,000, and for the past two years has averaged only \$3,500,000. The value of hides and skins imported into Japan in 1910 was \$686,626, and of sole leather \$530,196.

THE BLAST FURNACE REGENERATIVE STOVE.*

Regenerative stoves and their relation to blast furnace practice came in for special attention at a recent meeting in Pittsburgh of the Engineers' Society of Western Pennsylvania. The meeting was especially noteworthy for the large attendance and generous contributions of experts on blast furnace performance and centered about a paper presented by A. N. Diehl, superintendent of blast furnaces, Duquesne Works, Carnegie Steel Company, Duquesne, Pa. The paper in full, together with the discussion, has been printed in the Proceedings of the Society and from that source has been taken the following:

At the Duquesne blast furnace of the Carnegie Steel Company, we have at present, three different types of stoves: The center combustion, two-pass; side combustion, two-pass, and three-pass stoves. The construction of the two-pass side combustion, is possibly the simplest—a strong point in its favor. A number of these stoves have been in use for many years and have given good satisfaction. One of the earlier objections was the proper construction of the combustion chamber considerable trouble being experienced by the giving way of the walls, due to unequal expansion. Most of these difficulties have been overcome in the present construction. This stove is built up of standard size brick, so laid as to break all possible joints. We have also endeavored to cut out shapes wherever possible. The stove operates on dirty gas and has given us very good results.

Our two-pass, center combustion stoves are of the Kennedy type. The original stoves were constructed of concentric key boxes. We have since rebuilt some of these stoves with the standard size brick. They have individual stacks and the draft is unequally distributed; the checker work nearest the stack does most of the work until that portion becomes clogged with the dirt.

This lowers the efficiency of the stove to a considerable extent. The three-pass stoves are capable of giving the highest temperature, but are of a more complicated construction. A dome separates the second and third passes on top of the stove, and must be constructed to allow for expansion and contraction, which very often lead to cracks requiring attention. The blast is admitted at the top of the stoves through a mushroom valve, brought down over the dome through the third pass and through the second pass up under the dome again, where it is deflected through the combustion chamber. In case of cracks or leakage in the second or third passes, both the blast and air are bypassed, and go directly through the stoves without following their proper passages. This leads to great inefficiencies. We have experienced these difficulties in several instances.

A blast furnace will produce about 150,000 to 160,-

000 cu. ft. of gas per ton of iron, 10 per cent of which may be assumed as loss. One-third of the remainder will be burned in the stoves for the pre-heating of the blast, while the remaining two-thirds can be divided for power purposes and used at the boilers or for driving internal combustion engines. The gas, as it leaves the furnace contains a considerable quantity of dust, some of which is deposited in the dust catcher and mains, the finer portions being carried on to the point of gas consumption. This fine dust is carried into the stove with the gas, some of it impinging on the walls of the combustion chamber, clinkering, and forming heavy masses of cinder. Quite a lot of the dust passes through the combustion chamber and lodges in the checkers and in the bottom of the stoves. Cleaning doors are provided for the removal of such dirt when its removal is possible without taking off the stove. The dirt in the bottom of the second pass is very seldom fused, and can be scraped out readily, while that which remains in the checkers must be removed by means of iron weights or dillies.

If a stove is kept on too long, the checkers may become almost entirely closed up and the stove will neither absorb heat nor give it up. A glazing effect often takes place, which will also prevent the absorption of heat, and will lower the efficiency of the stoves. It is, therefore, desirable to keep the stoves as clean as possible. With the dirty gas we are forced to remove the dirt from the cleaning doors once a day, and take the stove off for complete cleaning about once every two months, which process requires about five or six days. The stoves have a checker area equal to 9 in. square which are frequently clogged to about 3 to 4 in. square, while some of them are closed completely. This is especially noticeable on stoves having a separate stack, the checkers on the side toward the stack closing first. It is thus very evident that for one-third of the time, the furnace is deprived of one-fourth of its heating surface capacity; the remaining three stoves, during such periods of cleaning, run down very rapidly. For this reason, in a number of recent constructions, five stoves have been advocated, so that when one is taken off for cleaning, the loss of heating surface is not so essential and the furnace is less affected. The alternative is the erection of four large stoves with the greater heating surface and smaller checker opening, say 6 in. square and using washed gas.

We have been using washed gas on four sets of stoves for about three years and at no time have we removed any stoves for cleaning. During times of suspension of operation for various reasons, we have gone into the stoves and do not find more than a coating of dirt on the top of the checkers, and in the checker walls. After a year and a half of service, one set of stoves was taken off and not more than 10,000 to 15,000 lb. of dirt removed from the entire set. The brick work in the combustion chamber, at the point of the flame impingement, showed a fused surface about 1 in. in thickness. At the bottom of the second pass was

*From the Iron Age.

found an impalpable deposit of a pinkish color of the following analysis:

Silica	22.80	
Iron	6.00	Fe ₂ O ₃ —8.57 per cent.
Manganese	1.50	Mn O ₂ —2.09 per cent.
Alumina	15.73	
Lime	21.42	
Magnesia	2.50	
	20.90	Potassium Oxide
	6.08	Ignition Loss.

The gas is washed through spraying tower washers, where it is at present cooled from 350 deg. to 5 or 6 deg. above the temperature of the washing water, and the dust removed to an average of about 0.2 of a grain per cubic foot. The year 1910 showed ingoing water to have an average temperature of 55 deg. and the temperature of the outgoing gas, 72.3 deg., or a difference of 17.3 deg. We have since re-designed the scrubbers, and now show only a difference of 5 deg. between the water and out-going gas. The results are obtained with the same water consumption per minute and a greater gas volume. The moisture, which will average 30 to 35 grains per cubic foot in the raw gas, is removed down to a point about $\frac{1}{2}$ grain above the saturation point, at the temperature of the gas as it leaves the scrubber,* 4 to 5 deg. above the temperature of the cooling water.

About 30,000 cu. ft. of gas are passed through each 12-ft. scrubber per minute, where it is repeatedly sprayed by means of a cut-off valve having a revolving core, the water spraying through nozzles and is broken up so as to bring it into very intimate contact with the gas. That this contact is attained, is evident by the close temperature of the gas to the entering cooling water. There are 815 gal. of water per minute used in each tower. The average since January 1, 1911, is 35 cu. ft. gas per gallon of water. There is some dirt deposited in the clean gas main, especially at such points where the main makes a bend, and these points must be cleaned out from time to time. If the gas is insufficiently cooled, it will pick up moisture to such an extent as to make it incombustible. In some cases, on a number of stove tests which we have run, the efficiency of the clean gas stoves is about 8 per cent higher than that of the dirty gas.

A comparison of stove equipments in the different plants shows a decided lack of uniformity in regard to heating surface required for different size furnaces. As an illustration, there are two modern plants, each having furnace bosh diameter of 22 ft. with 134,000 and 223,000 sq. ft. of heating surface respectively. Both furnaces should be capable of the same tonnage production. I should strongly advocate the latter figure as the better proposition, for with this heating surface, 1,100 or 1,200 deg. could be carried with little difficulty when furnace conditions would permit. Fire brick is a poor conductor of heat, and therefore the exposed area, or heating surface, should be as large as possible. The volume of brick work must be strong enough, however, to withstand all the strains to which it will be

subjected. It is evident that with a consumption of 5,000 cu. ft. of gas per minute a heating surface area too small would allow extremely high stack temperatures. This would introduce a loss which would not be present in case there was sufficient heating surface, yet at times, in order to get a high temperature in the stoves, this quantity of gas may be required.

The average blast furnace gas requires about 0.7 cu. ft. of free air for perfect combustion. This, however, does not allow for any variation and in practice should be carried to the proportions of about one to one. The air excess in this case will be slight and the loss in heat would be small, while sufficient oxygen is practically assured to meet all requirements in fluctuation of the constituents. It must be borne in mind that if dirty gas is used in the burner in the theoretical proportions, there is great danger of fusing the brick in the combustion chamber at the point of flame impingement. Heavy flue dirt clinker is also liable to form in the combustion well, clogging it up.

Draft should be symmetrical and uniform over the full area of the stove and the stack should be so placed and its communication to the stove should be such that this will be the effect. The feature of draft has called for considerable comment and opinion seems to differ as to the best location of the stack in relation to the stove. Some are favorable to the individual stack on the ground that the stoves are not subject to the discriminatory features of the single large stack, which is evidenced in its tendency to favor the closest situated stoves in the matter of draft intensity. On the other hand, opponents of the individual stack claim, that owing to the cooling of the stack during the period the stove is on the furnace, its influence is not properly exerted again until sometime after the process of regeneration has advanced and the stack has had an opportunity to become heated again. Too much importance cannot be attached to the necessity of having the draft symmetrical and uniform. The ill effects of not having it are many and may include such as: Local clogging in the regions where the draft is intensified; high velocity of combustion products with its consequent reduction of time contact and heating surface, intensified local temperatures producing glazing, vitrification and unequal expansion and contraction; highly heated surfaces confined to a comparatively small area and ultimately shifting the seat of operation to another point when resistance in the original path has become too great.

It might be added in passing that the superimposed stacks, those finding application in stoves of the three pass type, seem to have eliminated the difficulty of obtaining symmetrical draft, although having the disadvantages attributable to the cooling resulting during the period the stove is on the furnace. The ills above cited are particularly pronounced in the two-pass center combustion chamber, where communication to the

*From the Iron Age.

*Other information on gas cleaning at Duquesne, and also on blast furnace gas engines, under the authorship of Mr. Diehl, and others appeared in The Iron Age of July 6, 1911.

stack is so effected as not to be conducive to symmetry in draft.

Stack temperatures are dependent, first, upon the extent of heating surface; second, absorptive power and mass of brickwork; third, time contact, which is determined by the intensity of draft; fourth, the volume of the recuperative gases; and fifth, the blast. The time required by a unit volume of regenerative gases in passing through the stove will be considerably more than that required by the blast, the volume ratios of blast to heating gases averaging about four to five to one in the most approved practice. The item of stack temperature is one of the most important entering into stove operations and its influence upon the economies to be realized, not only on account of the enormous heat losses represented by abnormally high temperatures, but the deleterious effect upon chimney valves and seats where these are not water cooled. Heat losses in flue gases have been noted, constituting as high as 35 to 36 per cent of the total heat entering the stove in the fuel gas, which added to other losses encountered will often run up to 50 or 55 per cent of the total heat made available to the stove.

The tendency to conservation and the rapid increase in the cost of coal, consequently coke, has resulted in accentuating effort in the economical and efficient consumption of blast furnace gas. Consequently furnacemen have turned their attention to hot blast stove construction and the economical importance of its proper design, together with a conscientious regard for the quality of material that shall enter into its construction; all of which have a direct bearing upon the value and efficient consumption of fuel gases. Considerable attention has also been directed to the cleaning of gas as a means of economy in stove practice, a number of plants having extensive washing systems in operation.

Careful study of different tests made have clearly revealed some advantages in the use of cleaned gas for stove purposes, among which might be mentioned the possibility of higher blast temperatures, lower fuel consumption, uniformly higher thermal efficiencies, to which might also be added the absence of stove cleaning gangs and the interruptions of service consequent upon the use of dirty gas.

A concession has been granted by the executive authorities of Venezuela, in accordance with article 9 of the present mining code, to Dr. Rafael Max Valladares, giving him the right to explore the soil and subsoil of the States of Sucre, Monagas, Anzoategui, Nueva Esparta, Tachira, Trujillo, Merida, Zulia, Lara, Falcon, Carabobo, Yaracuy, and Delta del Orinoco, and afterwards to exploit, refine, export, and in general to dispose of as most convenient, but in accordance with the terms of his contract, all asphalt, petroleum, naphtha, or pitch which he may discover in his explorations. It is understood that this contract is made in the interest of American capitalists, and that a separate corporation will be formed to take over and work these concessions.

SPELTER PRODUCTION IN 1911.

The United States Geological Survey has just issued its annual advance statement of spelter production for 1911. This statement, prepared by C. E. Siebenthal, gives the final figures of output as made up from the smelter reports and is not subject to change unless an error is discovered in those reports. Preliminary estimates of the production of zinc, copper, lead, and some other metals in 1911 were published by the Survey January 2. These preliminary figures for spelter are shown by comparison with the final figures to have been in excess about 0.5 per cent of the total production.

The zinc ore mined in the United States is treated in three ways, being smelted to spelter (metallic zinc), converted into zinc oxide pigment, or exported from the country in the form of ore. The figures of spelter production therefore do not represent the complete zinc output of the different states. Missouri had, as usual, the largest output, though considerably less than in 1910, the yield being 127,540 short tons, compared to 140,652 tons in 1910 and practically the same in 1909. The states making the principal gains were California, which made its first important zinc output; Colorado, which nearly doubled its 1910 spelter output; Montana, which also nearly doubled its output and Illinois and Wisconsin, both of which made good gains. The total for these five states was 100,000 tons, compared with about 57,000 tons in 1910. Colorado ranked second in output of spelter, with Wisconsin and Montana following. If the exports of zinc ore and the zinc in pigments made from ore from the Franklin Furnace mine of New Jersey are taken into account, that state no doubt, as usual, ranked second in the production of zinc.

The production of spelter in the United States in 1911 from domestic ores was 271,621 short tons and from foreign ores 14,905 tons, a total of 286,526 tons, compared to 252,479 tons, 16,705 tons, and 269,184 tons, respectively, in 1910, a gain of 17,342 tons, or 6.4 percent. The world's output of spelter in 1911 was 974,385 tons, compared with 883,419 tons in 1910, a gain of 90,966 tons, or 10.3 per cent, showing that the United States did not make its quota of the world's gain. This country's share of the world's production in 1911 was 29.4 per cent, compared to 30.5 per cent in 1910 and 30.1 per cent in 1909.

Other tables given by Mr. Siebenthal show the production of secondary spelter from drosses, skimmings, and old metal, the consumption of spelter, and the imports and exports of ore, drosses and spelter. The imports of zinc ore showed a loss of about 25 per cent in zinc content compared with 1910. In all these tables, as well as those of spelter production, the figures are given for each year from 1906 to 1911, inclusive, in order that a fairly extended comparison may be possible.

A diagram covering the period from 1906 to 1911

inclusive shows by curves the average weekly price of spelter at St. Louis and at London, the average weekly base price of concentrates at Joplin, and the average weekly sales of zinc concentrates in the Joplin region. These curves show graphically the mutual relation of the London and St. Louis prices of spelter, and their relation to the price of concentrates in the Joplin region and to the production in that region.

A table of the zinc-smelting capacity of the country, with contemplated additions thereto for 1912, shows well the drift of current zinc smelter construction from the failing gas fields of Kansas to the coal fields of Illinois and the gas fields of Oklahoma. Illinois, with 21,544 retorts at the close of the year, will add 8,276 retorts in 1912. Oklahoma, with 15,620 retorts in 1911, will add 3,840 more in 1912. Kansas, with 31,378 retorts at the close of the year, plans no additional retorts and will probably in 1912 demolish some of the smelters not now actively operated. In Pennsylvania 2,880 retorts will be added in 1912, and 3,456 retorts were added in West Virginia in 1911. The total number of retorts at the close of 1911 was 85,018, to be compared with 94,328 retorts at the close of 1910. A total of 14,996 new retorts is planned for 1912.

A special and valuable feature of the report on the production of coal in 1910, issued by the United States Geological Survey, is a series of maps showing the known coal fields of the United States. These maps are printed on a scale of about 40 miles to the inch, and if pieced together would make a map the size of a large 6-foot wall map issued by the Survey. The various classes of coal areas are indicated by a variety of colors. The coal fields are shown to have a wide range, both as to character of coal—there being half a dozen grades from anthracite to lignite and as to present knowledge concerning the deposits, ranging all the way from the results of detailed surveys on which an almost exact estimate of tonnage can be based to the very general information that the area is underlain with coal-bearing rocks which probably contain coal that may or may not be found at minable depth. All this information is portrayed on the maps by colors or symbols. The maps show the county subdivisions in the several states and are therefore the most exact coal maps yet issued. Geologic work by the Survey in the coal fields is in constant progress, however, especially in the public-land states, so that even these maps are admitted to be imperfect, in the light of new information continually acquired. The Geological Survey has previously published at different times maps showing the coal areas of the United States, and it is probable that during the coming year the Survey will issue a still further revised edition of these maps.

The United States produced in 1911 \$20,000,000,000 worth of manufactures, of which \$1,000,000,000 worth were exported.

According to a statement which appeared recently in the Austrian press, the Government has bought the only radium mines at St. Joachimsthal, that were owned by private individuals. The purchase price is said to be 3,000,000 crowns (\$609,000) for the two mines "Sachische Edelleutestollen" and "Hergottszsche." During the last four years many efforts have been made by various financial institutions of Germany and France to purchase these deposits of pitchblende. It is estimated that the two mines will annually yield about 3 grams of radium and 3,000 kilos of uranium (salts), the latter valued at \$30,000. Their purchase by the Austrian Government gives it practically a monopoly on the radium output of the world and it is claimed that the annual production will be 5 grams (valued at \$400,000) as soon as the factory at Joachimsthal is in full operation, using the ore from the mines recently acquired in addition to that taken from the old silver mine which has been the source of supply.

The United States Geological Survey has issued the following publications dealing with potash discoveries, and which may be had from that bureau free. Bulletin 511: Alumite, a newly discovered deposit near Marysville, Utah; 64 pages, 3 plates. An account of the discovery of alunite near Marysville, Utah, and the development of the deposit as an important source of potash. The known occurrences of alunite, both in the United States and elsewhere, are mentioned and its commercial availability is discussed. Bulletin 512: Potash-bearing rocks of the Leucite Hills, Sweetwater County, Wyo.; 1 plate, 9 text figures. Describes briefly the rocks in the Leucite Hills, Wyo., and estimates the amount of leucite-bearing rock available and the approximate amount of potash that these rocks may yield as soon as a process is discovered by which the potash can be dissociated from the rock cheaply enough for commercial use.

An examination will be held April 3 at various cities throughout the country by the U. S. Civil Service Commission, Washington D. C., to secure eligibles from which to make certification to fill several vacancies in the position of laboratory assistant in ceramics in the Bureau of Standards, Department of Commerce and Labor, at salaries ranging from \$900 to \$1,200 per annum, and vacancies requiring similar qualifications as they may occur in other branches of the service. The person or persons appointed to this position will be stationed at the Pittsburgh, Pa., laboratory of the Bureau of Standards, and will assist in original investigations in the chemistry and physics of clays and clay products. The examination will consist of the subjects mentioned below: Practical and technical questions on ceramics, including also questions on geology and mineralogy, elementary physics, general inorganic chemistry, thesis or report (to be submitted to the examiner on the date of the examination), education and technical experience (in ceramics).

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NOTES AND COMMENT.

THE UNDERWOOD CHEMICAL SCHEDULE.

The New Underwood tariff bill covering the chemical schedule, now before the House of Representatives, seems to have found little favor in the trades affected. Commenting on the bill the Oil, Paint and Drug Reporter says:

"It is not going too far to say, however, that the apparent intent and purpose of the bill is different from that of any tariff measure adopted in recent memory. The idea of arranging a tariff schedule for the primary purpose of encouraging and protecting American industry by giving this country a shade the best of it in competition with European products, and incidentally to raise revenue, has apparently been abandoned. The bill has evidently been prepared—in keeping with the oft expressed principles of the chairman of the Ways and Means Committee—as a revenue measure. It is Mr. Underwood's idea that a tariff bill should always be a revenue measure primarily and that protection should be incidental. The changes in the schedule are recommended by the majority of the House because the country is put to the necessity of increasing its revenue from customs taxes, and it is calculated that this bill will add \$3,000,000 a year to the treasury's receipts. It cannot be assumed that it is the purpose of the drafters of the new bill to do a positive injury to any American industry, or that after

having such a result explained to them they will refuse to make modifications.

In many respects, however, the theory of the bill, as we said above, is an abandonment of existing tariff theories. The imposition of duties upon raw materials which are now free and which cannot be produced in this country, and in many instances in reducing the tax upon the finished product into which these materials are manufactured is a startling reversal of past practices. In many cases this may be disastrous to our home manufacturers. Take camphor as an example. Under the present law the crude gum is admitted free, while the refined pays a tax of 6 cents per pound; under the proposed bill the crude will pay duty at the rate of 3 cents per pound, while the rate upon the refined is reduced to 5 cents. In other words the present differential between crude and refined in favor of the American industry is 6 cents per pound; under the new law it will be but 2 cents per pound, and this, it is claimed by the manufacturers, will eliminate the American and turn the entire trade over to the Japanese refiners.

Among those engaged in the trades affected by the new measure there is little disposition at the present time to grow excited or to become alarmed. It is pointed out that it is a long and rocky journey between introduction by a committee in the House and enactment into a law by Presidential signature. The general plan is to issue no half-baked expressions of condemnation before thorough digestion of the measure and to rest easy upon the assurance that nothing will be done, even in the House, until the industries affected have been given a full opportunity to be heard. It is the general opinion that the Senate will be slow to adopt as radical a measure, even if the House should prove obstinate with regard to modification, and that the court of last resort—the President—has already laid down the dictum that no measure will be given official sanction which works an injury to American industry.

RECENT PATENTS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, 908 G Street, N. W., Washington, D. C.:

- 1,013,134. Process for **Welding Copper**. Roy C. Davidson, Fort Blakemore, Va. Patented Jan. 2, 1912.
- 1,013,181. Process of Making **Chlorosulfonic Acid**. August Klages and Hermann Volberg, Salbke, Germany. Patented Jan. 2, 1912.
- 1,013,404. Process of **Recovering Ammonia** from Gases. Heinrich Koppers, Essen, Germany. Patented Jan. 2, 1912.
- 1,013,458. Bleach-Out Process of **Colored Photography**. Kohn Henry Smith, Zurich, Switzerland, and Woldemar Merckens, Mulhausen, Germany. Patented Jan. 2, 1912.
- 1,013,511. Process of Producing **Pure Zinc Sulfid and Thiosulfates**, Pierre Pipereaut and Antony Vila, Paris, France. Patented Jan. 2, 1912.
- 1,013,538. **Floor Oil**. The oil consists of a solution of approximately 3 per cent of copper oleate in light

- petroleum oil, wax and a volatile hydrocarbon solvent. Carleton Ellis, Larchmont, N. Y., assignor to Ellis-Foster Company, a Corporation of New Jersey. Patented Jan. 2, 1912.
- 1,013,614. **Pyrites Briquet** and Process of Making Same. Jacob S. Robeson, Camden, N. J. Patented Jan. 2, 1912.
- 1,013,638. Process of Making **Oleum**. Thomas Lynton Briggs, Flushing, N. Y., and Henry F. Meriam, Summit, N. J., assignors to General Chemical Company, New York, N. Y., a Corporation of New York. Patented Jan. 2, 1912.
- 1,013,701. Manufacture of **Silicon Carbid.** Frank J. Tone, Niagara Falls, New York, assignor to the Carborundum Company, Niagara Falls, N. Y., a Corporation of Pennsylvania. Patented Jan. 2, 1912.
- 1,013,791. Process of Making **Hydrogen Peroxid** from Impure Persulfuric-Acid Solutions. Leo Lowenstine, Vienna, Austria-Hungary. Patented Jan. 2, 1912.
- 1,013,931. Reduction of **Silver Ores**. Colin G. Fink, Schenectady, N. Y., assignor to General Electric Company, a Corporation of New York. Patented Jan. 9, 1912.
- 1,013,984. Process of Making **Nitrates**. Carl Bosch and Wilhelm Wild, Ludwischafen-on-the-Rhine, Germany, assignors to Badische Anilin and Soda Fabrick, Ludwischafen-on-the-Rhine, Germany, a Corporation. Patented Jan. 9, 1912.
- 1,014,061. Process of Recovering **Copper** from its Ore. Henry H. Hess, Philadelphia, Pa., assignor to American Copper Extracting and Refining Company, a Corporation of Arizona. Patented Jan. 9, 1912.
- 1,014,062. Method of Producing **Zinc Oxid**. Harry H. Hughes, St. Louis, Mo. Patented Jan. 9, 1912.
- 1,014,254. Treatments of **Phosphates**. Nathaniel P. Pratt, Atlanta, Ga., assignor to Pratt Process Company, Atlanta, Ga., a Corporation of Georgia. Patented Jan. 9, 1912.
- 1,014,411. Process of Recovering the **Resinous Products** from Rosin Waste and the Like. David J. Ogilvy, Cincinnati, Ohio. Patented Jan. 9, 1912.
- 1,014,425. Manufacture of **Steel**. William R. Walker, New York, N. Y. Patented January 9, 1912.
- 1,014,454. Method of **Copperizing Iron**. William George Clark, Geelong, Victoria, Australia. Patented Jan. 9, 1912.
- 1,014,520. Utilizing Acid Sludge from **Refining Petroleum**. Clarence I. Robinson, West New Brighton, N. Y., assignor to Standard Oil Company, Bayonne, N. J., a Corporation of New Jersey. Patented Jan. 9, 1912.
- 1,014,560. Process of **Electroplating Aluminum** and its Alloys. Ernest Becker and Otto Becker, Iserlohn, Germany. Patented Jan. 9, 1912.

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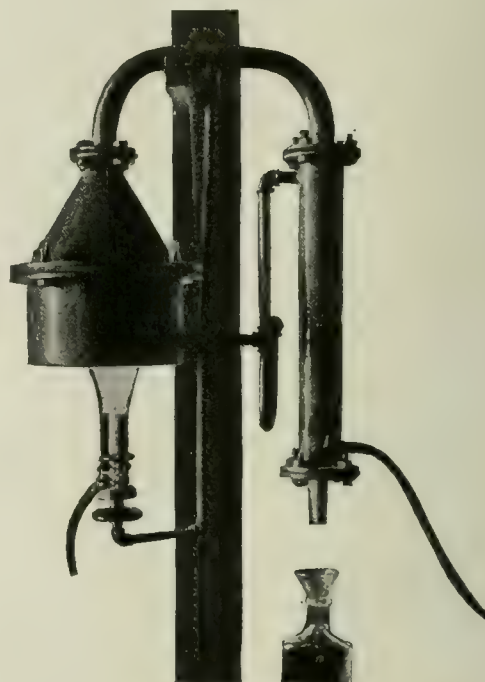
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No. 4.

LIQUEFIED PRODUCTS FROM NATURAL GAS: THEIR PROPERTIES AND USES.

By IRVING C. ALLEN and GEORGE A. BURRELL.

The chief purpose of the fuel investigations being carried on by the U. S. Bureau of Mines is to increase efficiency in the production and use of the mineral fuels in the United States. One of the investigations has for its object the determination of the economic value of the petroleum and natural gases, with special reference to the supplies in the public lands and the ascertaining of how these resources can be utilized in the industries with least waste and greatest efficiency. Technical Paper 10, dealing with this investigation, has been issued lately by the Bureau. This paper was prepared by Irving C. Allen and George A. Burrell, and from it has been abstracted the matter that follows:

In some of the petroleum fields, particularly in new fields, where the yield of oil and gas is abundant and the methods of handling are necessarily crude, considerable quantities of oil and great quantities of gas are wasted in various ways. In the older fields, where effective methods of handling and storage have been more fully developed, the loss is less. Yet in almost all the petroleum fields of the country more or less natural gas has been allowed to escape without restraint, and at some places enormous quantities have been wasted. Even today, in practically every oil field of the country, one can see many gas torches needlessly burning the entire 24 hours.

The handling of oil will not be discussed here. The handling of gas is a difficult matter, and consequently efforts at proper conservation have not as yet been entirely successful. In some fields the loss of gas is due to the fact that a ready market for the gas is not available or to the fact that the yield of the wells has declined so much that transportation of the gas through pipe lines is not profitable.

Natural gas may be divided into two great classes, (1) a so-called "dry gas," known and used for many years as the natural gas of commerce, and (2) a gas containing easily liquefiable vapors, which is known in the vicinity of the oil fields as a "wet gas." The latter class forms the basis for the so-called "natural gasoline" industry.

COMMERCIAL FRACTIONS OF NATURAL GAS.

By fractionating natural gas, either during or after liquefaction, four products can be commercially obtained. Roughly, these four products may be described as follows: (1) The gaseous product, the common natural gas of commerce; (2) the semiliquid product, known as the new "wild" product, which should be used only as a liquefied gas and should be held in high-pressure steel containers only; (3) the light liquid product, or light gasoline, used for blending with heavy naphthas; and (4) the heavy liquid product, or ordinary high-grade gasoline.

The first product, natural gas, is discussed in a subsequent section, as are also the third and fourth products.

The possibility of handling the second product in the way that Pintsch and Blau gases are handled, enabling small towns, hotels, and country estates to have the advantages of gas illumination, manifestly opens a new field of comparatively great importance in the natural-gas industry and should add materially to the investments made in the so-called "natural gasoline" industry.

THE DEVELOPMENT OF GAS LIQUEFACTION BY PRESSURE.

The liquefaction of gases by pressure is not a new industry, but only recently has its application to natural gas been recognized as practicable. Before discussing in detail the second, or semi-liquid product mentioned above a brief reference to the industry of manufacturing liquefied or compressed gas is deemed necessary.

In the early seventies, J. J. Coleman¹ successfully liquefied by pressure and cold the gases made by cracking the shale oils of Scotland.

By the processes of Blau,² Pintsch,³ Gray,⁴ Hastings-Brink,⁵ the Swiss Liquid Gas Co.,⁶ Schneider,⁷ Wil-

¹An apparatus for the continuous liquefaction of volatile gases generated from the distillation of bituminous shale. *Chem. News*, vol. 39, February 28, 1879, p. 87; *Mechanical Refrigeration*, vol. 2; reviewed in *Sci. Am.*, vol. 104, 1911, p. 27, and in *Oil and Gas Jour.*, vol. 9, June 1, 1911, p. 4.

²Herstellung eines Leuchtgases aus Destillatgasen. German patent 158,198; *Zeitschr. für angew. Chem.*, 1905, p. 671; *Blaugas*, *Seifens Zeit.*, 1907, p. 804; German patent (1905) 175,846; Kruger, F., *Blau Gas*, *Chem. Abs.*, vol. 2, 1908, p. 3402.

³Butterfield, W. J. A., gas manufacture, 1907, vol. 1, pp. 230-231.

⁴Gray, J. L., Apparatus for recovering light oils from natural gas, U. S. Pat. 933,976, 1909.

⁵Hastings, J., and Brink, A. W., Cooling gas and obtaining gasoline, U. S. Pat. 883,640 (March 31, 1908); *Chem. Abs.*, vol. 2, 1908, p. 2447.

⁶Mansfield, R. E., Manufacture of liquid illuminating gas in Switzerland, *Chem. Eng.*, vol. 16, p. 122; *Chem. Abs.*, vol. 4, January 10, 1910, p. 102.

⁷Schneider, W. P., Gas-liquefying apparatus for demonstration purposes, U. S. Pat. 984,030 (February 14, 1911); *Chem. Abs.*, vol. 5, April 20, 1911, p. 1353.

liams,⁸ Wolf,⁹ Wolski,¹⁰ and others gas is made by cracking oils in hot retorts. The gas is then washed and compressed into steel cylinders capable of safely withstanding the pressures developed. Several of these processes for manufacturing gases are commercially successful. They all entail the necessity, however, of first manufacturing the gases and then washing them.

The properties of the better known and more widely used illuminating gases are given in Table I.

TABLE I.—PROPERTIES OF CERTAIN MANUFACTURED GASES.

Name of gas.	Specific gravity (air = 1).	Heat value per cubic foot (0° C. and 760 m. m. pressure), B. t. u.	Candlepower (British) burning 5 cu. ft. per hour.	Unsaturated hydrocarbons, per cent.	Saturated hydrocarbons, per cent.	Hydrogen, per cent.
Pintsch gas ^a	0.60	1,500	45-50	35.65	45.37	12.44
Coal gas ^c	0.90	630	16	8.0	34.0	47.0
Acetylene ^d	1.125	1,555	150			
Carbureted water gas ^e	0.94		22	12.83	14.78	35.17
Uncarbureted water gas ^f	0.64				0.10	51.89
Ordinary natural gas ^g	0.64	1,189			99.00	
Liquid natural gas ^h	1.25	1,800-3,300	45-50		99.00	
Manufactured oil gas ⁱ	0.494	633	23	5.85	40.80	39.49
Name of gas.....	Carbon monoxide, per cent.	Carbon dioxide, per cent.	Oxygen, per cent.	Nitrogen, per cent.	Explosive limit.	
Pintsch gas ^a	0.60	0.74	2.00	3.00		
Coal gas ^c	9.0	1.1		2.3	7.1	19.0
Acetylene ^d					3.0	81
Carbureted water gas ^e	33.92	1.54		1.76		
Uncarbureted water gas ^f	40.08	4.80		3.13		
Ordinary natural gas ^g					5.5	12.0
Liquid natural gas ^h					3.0	7.0
Manufactured oil gas ⁱ	4.50	2.75	0.85	6.01		

^aHills, H. F., Gas and gas fittings, 1902, p. 52.

^bApproximate.

^cBurrell, G. A., Average result of several analyses of coal gas.

^dButterfield, W. J. A., The chemistry of gas manufacture, 1898, p. 393.

^eButterfield, W. J. A., The chemistry of gas manufacture, 1907, vol. 1, p. 224.

^fLewes, V. B., Liquid and gaseous fuels, 1907, p. 220.

^gBurrell, G. A., Average results of several analyses of West Virginia and western Pennsylvania gases.

^hBurrell, G. A.

ⁱCalculated.

^jAllen, I. C., Average results of several analyses of manufactured petroleum gas used on the Pacific coast.

The illuminating values given above are those of the ordinary naked flame, without a mantle. How greatly a mantle increases the light is shown in Table II.

According to A. C. Humphreys,¹¹ "The use of man-

⁸Williams, C. H. G., Liquid hydrocarbons from compressed petroleum gas, Jour. Soc. Chem. Ind., vol. 3, August 29, 1884, p. 437.

⁹Wolf, L., Liquefied oil gas; Chem. Abs., vol. 5, January 20, 1911, p. 372.

¹⁰Wolski, —, Liquefying natural gas by the Linde process, Petroleum Rev., vol. 13, p. 428.

ties in the Pintsch system increased the lighting effect about four times, and with the same storage capacity the length of period between fillings was increased 60 per cent."

Acetylene has been burned with increased efficiency in mantles but because of the high luminosity and whiteness of the flame itself and because of obstacles yet to be overcome in using mantles, the use of mantles with acetylene has not been generally adopted.¹¹

According to tests conducted by Drs. F. Schneiwind, Chas. E. Chandler, E. G. Love and H. Schweitzer¹² Blau gas has a specific gravity of 0.940, a heating value of 1731 B. t. u. and an illuminating value, when burned in an inverted mantle, of 108 standard candles. It is further stated that 2.52 kilograms of oil will produce 1 kilogram of the gas.

Early Attempts to Liquefy Natural Gas.—The liquefaction of natural-gas products was early recognized as of possible commercial importance.

Pasenmeyer¹³ and others procured gasoline in commercial quantities near Titusville, Pa., in 1904, by collecting the condensations in the gas mains. The yield of gasoline so obtained was further increased in 1905 by chilling the pipes with cold water, and from 1905 to 1909 the yield was still further increased by

TABLE II.—COMPARATIVE ILLUMINATING POWER OF GAS BURNERS.

Flat flame, burning 5 cu. ft. per hour. British candlepower.	Burner equipped with mantle, burning 5 cu. ft. per hour. British candlepower.
23.1	117.3
17.9	90.3
16.2	87.9
14.6	84.4
13.5	81.9

¹¹Hills, H. F., Gas and gas fittings, 1902, p. 106.

the establishment of small, low-pressure, single-stage compressing plants. In the last few years the industry has made remarkable strides.

Up to the last two years the general practice in the manufacture of liquid natural gas was to make the product by compression of the gas in single-stage compressors operated at a pressure of 150 to 300 lbs. per square inch. The one product thus obtained, so-called "natural gasoline," was run into a tank and "weathered." The weathering consisted in allowing the lighter portions to volatilize spontaneously and escape into the open air until such time as the boiling away of the liquid had practically ceased. Thus the process involved a loss of 25 to 50 per cent, or even more. This loss was an absolute waste, not only of power and of cost of operating the engines and compressors but of the product itself.

Later Improvements.—The next step in the industry was to pass the waste gases (of which only the small quantity used for power had been utilized) from the

¹¹Lectures on illuminating engineering, delivered at the Johns Hopkins University, October and November, 1910, under the joint auspices of the university and the Illuminating Society; 1911, p. 208.

¹²Prospectus of the Blau Gas Company, pp. 42-43.

¹³Taylor, Frank H., Early history of utilization of gasoline from natural gas, Oil City Derrick, May 6, 1911, p. 9; Oil and Gas Jour., vol. 9, May 11, 1911, p. 20; The gasoline from natural gas industry, Oil and Gas Jour., vol. 9, March 2, 1911, pp. 2-6; Petroleum, March 17, 1911, vol. 6, p. 896.

single-stage compressor through a higher-stage compressor, thereby getting a second and more volatile product—a "wilder" liquid—which was run back into the first tank and mixed with the first or heavier condensate. This mixture was then again weathered to a safe degree, whereby it lost the greater part of the more volatile product that had been condensed in the second stage.

Recently the process has been improved another step, in that the first stage compressor product is run into one tank and handled as ordinary gasoline; the second stage compressor product is run into a second tank and handled as a lighter gasoline,¹³ with which the heavy refinery naphthas can be enriched or enlivened.

The last-mentioned method of using the second stage compressor product should receive wide recognition, and a market for the product should develop that would be no mean factor in the industry. Blending in the proportions of, say, 1 part of the product to 4 or 5 parts of the refinery naphthas makes these heavy naphthas more volatile and of greater value as fuel for automobiles; it also greatly increases their general usefulness. The proportions to be used in blending, however, must be determined more definitely by test.

Practical Deductions.—The natural gas of this country frequently contains light products that do not condense in the second-stage compressor, and for which it is practicable and necessary to install three, four, and even higher stage compressors. These light products—true gases at ordinary temperatures and pressures—can be compressed and liquefied, but the liquid gases so obtained must be handled as gases and not as oils. The mistake heretofore made in the "natural gas gasoline" industry, as some have recognized, has been the attempt to handle the light gaseous products as oils and not as gases. Until the manufacturers of this lightest third or fourth stage compressor product recognize its gaseous nature, the absolute necessity for insuring the safety¹⁴ of the public involves certain restrictions in its transportation, and not until the realization that this extremely volatile liquid should be handled only in strong steel containers capable of withstanding high pressures will it be transported with safety.

CRUDE NATURAL GAS.

Constituents.—The natural gases of the Appalachian oil fields are not the complex mixtures generally reported, but are composed of the paraffin hydrocarbons with carbon dioxide and nitrogen as impurities. The gases that issue under considerable pressure or that are produced in quantities sufficient to justify piping for

distant consumption consist principally of methane and ethane, the methane predominating. Small quantities of the higher paraffin hydrocarbons are also believed to be present. Olefin hydrocarbons and carbon monoxide have not been detected in the samples thus far examined by the Bureau of Mines, and oxygen appears to be present only when the sample has been taken in a faulty manner and air has been admitted.

Natural gases that issue from old wells in which the original rock pressure has diminished contain higher members of the paraffin series, such as propane and butane, in larger quantities, and when a pressure below atmospheric is applied to the wells still larger quantities of the higher paraffins are obtainable. For example, in the oil pool surrounding Tidioute, Pa., a pool that has produced oil and gas for many years, the gas is now drawn from the wells under a pressure 12 to 13 lbs. below that of the atmosphere, and a liquid product is obtained therefrom without the use of artificial pressure or cooling appliances.

Some natural gases in the United States contain methane only, and such gases are not adapted to the production of gasoline or liquid gas. Gases that contain no paraffin hydrocarbons higher than ethane require a pressure of 600 to 700 lbs. to the square inch at 35° C. for the liquefaction of the ethane. At lower temperatures less pressure would be required. Since these high pressures are not used in the commercial plants producing gasoline from natural gas, ethane is not being liquefied in such plants, but a partial solution of the ethane in those paraffins that are liquefied undoubtedly takes place.

Propane and butane are on the dividing line between gases and liquids and must be handled as such—that is, as heavy gases or as very volatile liquids—and if held must be imprisoned in strong containers only. Pentane, hexane, and heptane are liquids under ordinary conditions and comprise ordinary gasoline.

Present Waste.—The vapors accompanying natural gas are clean and are ready for compression. They are analogous to the manufactured products, but have the great advantage over the latter of being ready made. However, they are at present in a great measure lost to the industries. The vapors should be compressed, as previously stated, but instead of being run into an open tank, or into a closed tank and weathered from it, with a corresponding loss, they should be run into steel containers and held there under compression. Such containers, capable of withstanding 3,000 lbs. pressure, may be procured from several commercial firms. They may be transported to wherever gas of high heating or illuminating power is required. Liquefied gases of all kinds, such as carbon dioxide, hydrogen, oxygen, and acetylene, have been handled successfully in such containers for a number of years.

Proposed Utilization of Products.—Some of the products of natural gas which are now going to waste could be compressed into containers and could be handled as gases. The process has been developed for

¹³Fithian, Dr. Edwin J., The fractionation of natural-gas gasoline; Natural Gas Association, sixth annual meeting, at Pittsburgh, Pa., May 16, 1911. Natural Gas Journal, August, 1911, pp. 16-17.

¹⁴Dunn, B. W.: Gas gasoline safety standards, Oil and Gas Jour., vol. 10, June 22, 1911, pp. 16-18; Standards for gasoline safety, Oil City Derrick, June 19, 1911, p. 8; Proposed regulations of Bureau for the Safe Transportation of Explosives and other Dangerous Substances for the shipment of liquids flashing below 20° F., Nat. Petroleum News, vol. 2, February, 1911, pp. 10-11.

other gas industries, but its promise as a profitable commercial enterprise in connection with the development of the new product has only recently been recognized.

The multiple-stage compressor may be used for obtaining a number of products, or the single-stage compressor may be used for obtaining one product; then, by allowing this "wild" product to escape from a common container into a second, a third, and a fourth container, under partial pressures, it may be separated or fractionated into a second, a third, and a fourth product. This compression and later separation or fractionation of a common "wild" product into several products is, however, a waste of power, as ordinarily the gas should be compressed through several stages directly into its several products.

EXPERIMENTS IN LIQUEFYING CRUDE NATURAL GAS.

Experiments in the production of liquid gas were made at an experimental test plant installed by the authors at the compressing plant of the Penn Gasoline Co., Follansbee, W. Va. The test plant consisted of a small gas engine, a small compressor, cooling coils of ordinary 1-in. iron pipe immersed in a shallow tank for holding the cooling liquid, and a storage tank made of heavy 6-in. steel tubing. Pressures up to 600 lbs. were obtained, and with the use of ice and liquefied gas prepared in the adjoining compressing plant, the product was cooled to 2° C. as it entered the storage tank. The crude gas as it came from the wells was subjected to different pressures and temperatures, and the amount of liquid produced was measured. From lack of an experimental meter of sufficient capacity, no measurements were made to ascertain the quantity of crude gas liquefied. As all the gas was liquefied, excepting a small leakage, it was assumed that the subsequent volatilization of the compressed product in the laboratory gave this value. Samples of the liquid material were collected in stout steel cylinders, weighed, and passed through a small experimental meter to determine the gas yield per gram of liquid.

Yield of Liquid Products.—Table III gives the results of these experiments, in which practically complete liquefaction was obtained:

TABLE III.—RESULTS OF COMPRESSION AND COOLING TESTS OF NATURAL GAS.

Pressure exerted in liquefaction (pounds per square inch).	Temperature of cooling coil at entrance to storage tank, °C.	Volume of gas per gram of liquid, c. c.
415	2.0	600.9
430	4.0	
506	9.1	
600	77.5	478.1

A pressure of 415 pounds at 2° C., of 430 lbs. at 4° C., of 506 lbs. at 9.1° C., or of 600 lbs. at 77.5° C., liquefies practically the total volume of the gas being compressed. Assuming the liquid to be a mixture in which the propane and ethane predominate, as indicated below, 1 gram of liquid will yield 500 to 600 cubic centimeters of gas at 0° C. and 760 millimeters pressure; that is, 1 gallon of liquid will yield approximately 50 cubic feet of gas.

Properties of Crude Natural Gas and of the Volatilized Liquid Products.—Table IV shows the composition of crude natural gas and of the volatilized liquid products of compression.

Analysis No. 1 is of the natural gas of Pennsylvania and West Virginia, which is used at Pittsburgh for heating and lighting purposes. This gas is not adapted to the production of gasoline, but the analysis is inserted here for comparison with the Follansbee gas, which was used in the production of gasoline at the plant before mentioned.

Analysis No. 2 shows the composition of the crude natural gas from the wells at Follansbee before being subjected to compression at the commercial plant there.

Analysis No. 3 shows the composition of the gas left after the initial compression of 50 lbs. to the square inch.

Analysis No. 4 shows the composition of the gas left after the final compression of 250 lbs. to the square inch. This residual gas is turned into the mains for

TABLE IV.—PROPERTIES OF CRUDE NATURAL GAS AND OF THE VOLATILIZED LIQUID PRODUCTS OF COMPRESSION.
[G. A. Burrell, analyst.]

Analysis No.	Kind of gas.	Specific gravity ^a (air = 1)	Heating value per cubic foot (0° C. and 760 mm. pressure), B. t. u.	Methane, per cent.	Ethane, per cent.	Propane, per cent.	Butane, per cent.	Nitrogen, per cent.
1	Natural gas (Pa. and W. Va.)	0.64	1,189	83.0	16.4	..	..	0.6
2	Natural gas (Follansbee, W. Va.)	1.39	2,468	..	21.8	77.7	..	0.5
3	Residual gas after 50-lb. compression product has been removed..	1.35	2,364	..	34.9	64.6	..	0.5
4	Residual gas after 250-lb. compression product has been removed..	1.15	2,008	..	79.4	20.0	..	0.6
5	Gas from liquefied gas (400 lbs. pressure, 0° C.)	1.01	1,808	3.8	95.0	..	..	1.2
6		..	2,066	..	72.5	27.0	..	0.5
7		1.28	2,214	..	52.1	46.9	..	1.0
8		..	2,621	..	1.1	98.0	..	0.9
9		1.02	1,816	4.7	94.9	..	..	0.4
10		..	1,925	..	89.3	9.9	..	0.8
11	.. do	..	2,108	..	67.0	32.5	..	0.5
12		..	2,162	..	59.4	39.8	..	0.8
13		..	2,708	..	..	89.2	9.9	0.9
14		..	3,221	..	..	24.0	75.0	1.0

^aBy effusion method.

consumption in the ordinary manner. Its high quality is evident, it having almost twice the heating value of the natural gas used in Pittsburgh.

The four analyses next following, Nos. 5, 6, 7, and 8, show the composition of the liquid gas as obtained from the experimental plant erected by the authors at Follansbee. A cylinder of the liquid gas was taken to the bureau laboratories and connected with a small experimental gas meter. The yield of gas was measured and four samples taken at regular intervals. This test was not finished owing to an accident to the meter.

The next six analyses, Nos. 9, 10, 11, 12, 13 and 14, cover the analysis of the gas, from the first portion

released to the last that came from the cylinder. The gas was taken from the top of the cylinder, and the first or more volatile portion approximated ethane in composition. The gases next volatilized contained less ethane and more propane, and, finally, in the last portion butane predominated.

These analyses are approximate, and do not give a definite division of the paraffins. No method is known of separating individual paraffins in a mixture of several, unless means be employed whereby the total gas is liquefied and the different paraffins separated by fractional distillation.¹⁵ In gas analysis no absorbent is known that will quantitatively separate one of the paraffins from a mixture of several and not act upon the others; consequently paraffins are determined as a whole by combustion, and their percentage found by a calculation made from the contraction in volume and the carbon dioxide produced by the burning. By this method the two predominating paraffins are shown, but a small quantity of the others which may exist is not made apparent. For instance, the crude gas that the authors compressed, analysis No. 2, is shown to consist of ethane and propane only. That methane and butane are also contained therein is evidenced by analysis No. 5, in the series of four, and analyses Nos. 9 and 10, in the series of six. Undoubtedly pentane and hexane were also present. Methane was found in the first portions of gas from each cylinder, but was not present as a liquid in the cylinders, because pressures sufficient to liquefy it were not obtained in the experiments. It was simply dissolved to a certain extent in the other paraffins.

The total paraffin hydrocarbons, as shown by the analyses, are correct, but as stated before only the predominating ones are disclosed by combustion analysis. The methods and apparatus used in the analysis of natural gas will be fully described in a forthcoming bulletin of the Bureau of Mines, entitled "Methods and Apparatus for the Examination of Mine Gases and Natural Gas." The apparatus is believed to be superior to the types ordinarily used for the analysis of natural gas.

With the exception given in the first analysis, the heating values were calculated from the chemical analyses, and are gross heating values.

The heating value of sample No. 1, as determined in a Junker calorimeter, checked the calculated heating value within 10 B. t. u. A burner could not be found, however, that would develop the maximum heating value as calculated from the analysis,¹⁶ and all of the determined heating values of the remaining samples in the above table were about 300 B. t. u. lower than the calculated values.

Properties of the Paraffins Ordinarily Present in Natural Gas.—For comparison with the analyses described above, the properties of the paraffins ordinarily present in natural gas are given in Table V.

CHARACTERISTICS OF LIQUEFIED NATURAL GAS.

The liquefied-gas product obtained from the third and fourth stage compressor product previously mentioned (but not the heavier first-stage compressor product, that which ordinarily remains after weathering) begins to boil at about -40°C. , and at its boiling point has a specific gravity of approximately 0.63. Its coefficient of expansion is estimated to be 0.0009 per 1°C. Its specific gravity at 15°C. would, therefore, be approximately 0.57 to 0.58.

TABLE V.—PROPERTIES OF THE PARAFFINS ORDINARILY PRESENT IN NATURAL GAS.

Name	Formula	Boiling point, ^a °C.	Specific gravity.		Weight of 1 liter, grams	Heating value per cubic foot, at 0° C. and 760 mm., B. t. u.	Theoretical volume of air necessary to burn 1 cu. ft. of gas, Cubic feet
			At different temperatures (water = 1)	At 760 mm. and 0° C. (air = 1)			
Methane	CH ₄	-160	0.415 at -160° C.	0.5529	0.7150	1,065	
Ethane	C ₂ H ₆	-93	1.0366	1.3404	1,861		
Propane	C ₃ H ₈	-45	1.5204	1.9659	2,654		
Butane	C ₄ H ₁₀	1	2.004	2.5914	3,447		
Pentane	C ₅ H ₁₂	36.4	.627 at -14° C.			4,250	
Hexane	C ₆ H ₁₄	68.9	.658 at -20° C.			5,012	
Heptane	C ₇ H ₁₆	98.4	.683 at -20° C.				
Name	Formula	Boiling point, °C.	Specific gravity.		Weight of 1 liter, grams	Heating value per cubic foot, at 0° C. and 760 mm., B. t. u.	Theoretical volume of air necessary to burn 1 cu. ft. of gas, Cubic feet
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Heptane	C ₇ H ₁₆	98.4	.683 at -20° C.				
Name	Formula	Boiling point, °C.	Specific gravity.		Weight of 1 liter, grams	Heating value per cubic foot, at 0° C. and 760 mm., B. t. u.	Theoretical volume of air necessary to burn 1 cu. ft. of gas, Cubic feet
			At different temperatures (water = 1)	At 760 mm. and 0° C. (air = 1)			
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^aHolleman, A. F., Organic chemistry, edited by A. J. Walker, 1910, p. 41.

^bIdem.

^cHempel, Walther, Methods of gas analysis. English translation, by L. M. Dennis, 1910, p. 482.

^dLandolt and Börnstein, Physikalisch-chemische Tabellen, 3rd edition, pp. 416, 425 (by J. Thomsen).

^eOther authorities give -17°C.

^fHunt, Charles, Gas lighting, vol. 3 of Chemical Technology, by C. E. Groves and Wm. Thorpe, 1904, p. 202.

^gWright, L. T., Jour. Chem. Soc., vol. 47, 1885, p. 200.

^hLandolt and Börnstein, Physikalisch-chemische Tabellen, 1905, p. 185 (by Dewar).

ⁱBörnstein, F., Handbuch der organischen Chemie, 3rd edition, vol. 1, p. 101.

^jLandolt and Börnstein, Physikalisch-chemische Tabellen, 1905, p. 185 (by Olszewski).

^kPhillips, F. C., W. Va. Geol. Survey, Oil and gas levels, vol. 1 A, 1904, p. 515.

^lFrankland, P., Jour. Chem. Soc., vol. 47, 1885, p. 235.

^mLandolt and Börnstein, Physikalisch-chemische Tabellen, 1905, p. 182 (by Dewar).

ⁿIdem, p. 182 (by Olszewski).

^oIdem, p. 185 (by Olszewski).

When this liquid is confined the pressures generated by increasing the temperature are approximately as shown in Table VI.

From the above data the internal pressure generated

¹⁵Tests of more detailed fractionation are now being made at the Bureau of Mines laboratories.

¹⁶W. J. A. Butterfield, The chemistry of gas manufacture, 1907, vol. 1, p. 233.

by this volatile liquid, or the so-called "wild" product, is seen to reach 755 lbs. per square inch at 55° C. This pressure is probably the maximum obtainable with the very light, or "wild," liquefied natural-gas product having a specific gravity of 0.60 at 15° C., or 100° F. at 60° F. The fact that several gases, under pressures in excess of 150 atmospheres, or 2,250 lbs. per square inch, are successfully handled in commerce daily and have been so handled for a number of years, and the fact that this "wild" gas generates an internal pressure of only 755 lbs. at 55° C., or 133° F., which would be an excessively high summer temperature, show that the ordinary handling of this liquefied gas in summer as well as in winter is simple and practicable, and can be done with appliances already developed and on the market. The margin of safety is ample.

There is no difficulty nor secrecy in the production and use of the liquefied natural-gas product. The third or fourth stage compressor product must, however, be treated as liquefied gas, and no attempt should be made to handle it as an oil.

It is important to note that many natural gases will not yield liquefied products by compression under ordinary commercial conditions, and the prospective investor is therefore cautioned to ascertain the nature of the vapor content of the gas under consideration before investing in an expensive compressor plant.

EFFICIENCY OF LIQUEFIED PRODUCT FOR DEFINITE USES.

Illumination.—When lighted in burners the liquefied product gives a flame much like that of the ordinary

TABLE VI.—PRESSURES GENERATED BY HEATING GASOLINE AND CONFINED LIQUEFIED NATURAL GAS.

Temperature. °C.	Refinery gasoline (80° B.). Pounds.	Pressure generated at— Natural gasoline obtained at—		
		50 pounds pressure. Pounds.	250 pounds pressure. Pounds.	400 pounds pressure. Pounds.
0	0	..	107	360
5	0	9	117	375
10	0	12	130	398
15	0	16	144	423
20	3	20	154	453
25	5	25	175	482
30	10	30	193	510
35	16	34	210	545
40	26	40	231	585
45	41	46	251	630
50	92	52	275	690
55	350	58	..	755
60	..	65	..	..

natural gas of commerce, but slightly yellower or smokier, and does not burn so readily in burners with lava tips. Its flame in a Bunsen burner is short but very hot, and it burns better in the short inverted Welsbach mantle than in the longer upright mantle. The highest economy in its use for illuminating purposes will be attained with inverted burners provided with mantles, burners of this type being especially adapted for gases of high heating value.

Heating.—The Méker burner, or a similar burner with a small gas orifice and a large air supply, is well adapted for complete combustion of the gas, as is also the Matchlet blast burner. With oxygen in the oxy-gas burner the liquefied product makes a hot, steady flame, and can be used for a number of purposes, such

as brazing, and for operations in which intense local heating is desired.

Because of its high carbon content, the perfect combustion of the gas requires considerably more oxygen than the ordinary gas burners are capable of admitting. A cubic foot of ordinary natural gas requires 10 or 11 cu. ft. of air for its complete combustion, but propane and butane, the two richest constituents in the liquid gas, require respectively about 25 and 32 cu. ft. of air.

This product of natural gas is equal in quality to any of the similar manufactured gases; it is very clean and pure and can be handled in the same way as they are. The containers can be easily transported, and the turning of their valves makes a supply of gas available. The liquid gas should be used from the bottom of a container, in order that the burners may be supplied with a homogeneous mixture; the gas should not be taken from the top, because with such an arrangement constant adjustment of the air supply is necessary.

Power.—In order to determine the feasibility of using for power purposes the gas under discussion, a short test was made with a gas engine. A 10-H. P. two-cycle gas engine provided with a prony brake for absorbing the load, and equipped with the usual electric ignition, was used. The high-pressure cylinder containing the liquid gas was connected through a reducing valve to a small cylindrical receiver, capacity about 3 cu. ft., in which a pressure of about 3 ins. of mercury was maintained; from this receiver a pipe connection led directly to the engine. No attempt was made to determine accurately the fuel consumption per horsepower-hour, nor to find the compression best adapted for the fuel, the test being made simply to determine the behavior of the gas in a commercial type of engine.

The test was of 30 minutes' duration; full load was easily maintained, and there was no difficulty whatever in keeping the engine up to speed. Throughout the test the engine ran easily, giving no indication of overload; there were no back fires nor preignitions. The indications were that the gas would make a satisfactory gas-engine fuel. The brake horsepower (10.69) during the run was calculated from the following data:

Average revolutions per minute.....	277.7
Length of brake arm, feet.....	5.25
Weight of brake arm, pounds.....	36.5
Total weight on scales, pounds.....	75
Effective weight on scales, pounds.....	38.5

A cylinder of the liquefied gas was also used for driving a 30-horsepower automobile. A most satisfactory run was made for a number of miles, although no attempt was made to determine the efficiency developed, the only result desired being to demonstrate that the compressed product could be used for automobile propulsion. It was noted that the gas escaping from the container through the regulating valve supplying the engine became chilled and that considerable frost collected over the surface of the valve. This effect would, in general practice, soon freeze the liquid in the valve and clog the pipe entirely. By installing

this valve near the engine exhaust the freezing may be prevented.

HANDLING OF NATURAL-GAS PRODUCTS OTHER THAN LIQUEFIED GAS.

High-Grade Gasoline.—The third previously mentioned product of crude natural gas, light high-grade gasoline, is a material that, by co-operation with the refiners of petroleum, can be utilized for blending with the heavy naphthas, thereby improving the latter and making them more suitable for the propulsion of high-speed automobiles. This use will materially improve the market for the heavy naphthas, and also widen the field of usefulness for the new compression product. The proportions in which the blending should be made to insure some degree of permanency have not yet been established.¹⁷

Ordinary Gasoline.—The fourth product from compressing crude natural gas, ordinary gasoline, may be handled in the usual way, and need not be discussed in this paper.

POTASH SALTS: SUMMARY FOR 1911.*

By C. W. Phalen.

SOURCES OF POTASH SALTS.

The possible sources of potash salts in the United States are as follows: (1) Saline residues; (2) natural and artificial bitterns; (3) alunite and similar minerals; (4) the igneous rocks containing as a lower safe limit at least 6 per cent of potash (K_2O); (5) the greensand marls of Kentucky, New Jersey, Tennessee and probably other states; (6) organic sources, including wood ashes, beet sugar molasses and residues, wool scourings and seaweed.

During 1911 the search by the United States Geological Survey for potash salts covered several fields, as follows: (1) Deep drilling for saline residues; (2) the collection and examination of natural and artificial brines and bitterns; (3) the examinations of deposits of alunite and other minerals containing potassium; (4) the examination of certain occurrences of igneous rocks known to contain large quantities of potash.

Besides the work of the Survey, the Bureau of Soils of the Department of Agriculture has taken up the systematic study of the seaweeds or kelps of the Pacific Coast. The recent report¹ issued by the Bureau of Soils on the fertilizer resources of the United States covers the entire field. The Bureau of Soils also co-operating in the study of the bitterns referred to under (2) above. It has also undertaken a field survey of the desert basins of the arid states of the West in search of fertilizer materials, and laboratory investigations are now under way (1) to ascertain the effect of water and other reagents on the potash feldspars and other silicates, and (2) in the study of aqueous

(water) solutions of mixtures of potassium and sodium salts.

Private persons are also interested in all these fields of search, and numerous investigations are known to be in progress which have for their object the discovery of a cheap and ample supply of potash salts.

The different phases of the work that has been in progress during 1911 and to date in 1912 are described in detail below.

DEEP-DRILLING EXPLORATIONS.

Examples of the occurrence of potash salts on a large scale are comparatively rare. Besides the German deposits, the only known noteworthy occurrence in the world is that at Kaluszc, Galicia. The great classic example is that occurring on the inner side of the Magdeburg-Halberstadt Permian basin in central Germany. At the southeastern end of this basin potash salts were discovered by drilling about the middle of the last century and were first mined at Stassfurt and Egehn. The deposits are usually referred to as the Stassfurt deposits.

It is possible that salts of the Stassfurt type found in Germany may also be found in the United States. The only method of finding these salts is by deep drilling. As a guide to this deep drilling the systematic examination of the brines and bitterns of the United States will prove helpful, for it will indicate possibly where deep drilling may be undertaken with the best chances for success. Both these phases of work were taken up at the very outset of the potash salts investigation by the United States Geological Survey.

Deep-drilling explorations by the survey were begun near Fallon, Nev., October 6, 1911, under the direction of H. S. Gale.¹ The reasons for choosing this place as the site of first drilling operations have been amplified in a former publication of the survey² and will only very briefly be given here.

Fallon, Nev., is located in the Great Basin region of the western United States. The region has at present no outward drainage, nor has it had for long periods of time. Its system of ancient lakes is included chiefly within Utah, Nevada, and California, but portions are also included in Oregon, Idaho and Wyoming. Its history has been worked out by Russell³ and Gilbert.⁴ In his geologic history of Lake Lahontan, one of the Quaternary lakes of the Great Basin, Russell presents evidence favoring the possible existence of saline deposits in this region.

Lake Lahontan flooded the valleys of northwestern Nevada in very recent times, geologically speaking, but it has now disappeared. It covered an area of 8,422 square miles and was 886 ft. in depth in the deepest part. It is not known to have ever overflowed. It had two high-water stages separated by a period of

¹Gale, H. S., The search for potash in the United States: Bull. U. S. Geol. Survey No. 530-A, 1911, 29 pp.

²Bull. 530-A.

³Russell, I. C., Geological history of Lake Lahontan, a Quaternary lake of northwestern Nevada: Mon. U. S. Geol. Survey, vol. 11, 1885.

⁴Gilbert, G. K., Lake Bonneville: Mon. U. S. Geol. Survey, vol. 1, 1890.

¹⁷The Bureau for the Safe Transportation of Explosives and other Dangerous Articles is now engaged on these tests.

*Abstract of advance chapter from Mineral Resources of the United States, calendar year 1911.

¹A preliminary report on the fertilizer resources of the United States; S. Doc. 190, 62d Cong., 2d sess.

drying or desiccation. The first great rise was also preceded by a period of desiccation. During the second period of flooding the lake rose higher than during the first. It then evaporated completely to dryness. The present lakes of the basin are of comparatively recent date and their water is fresh, for the reason that the salts deposited when the Quaternary lake evaporated were buried or absorbed by the clays and marls that occupied the bottom of the basin.

It is a rule that all lakes which have no outlet become finally charged with mineral salts. Examples of saline deposition resulting from the evaporation of inclosed lakes are common in the Great Basin. In the Lahontan basin deposits of this character resulting directly from the evaporation of a former lake are nowhere to be found. Wherever the lake sediments have been examined, however, they have been found to be charged with salts of presumably the same character as those that were most common in the waters of the former lake. It is beneath the level floors of the valleys and lake basins that the most soluble salts formerly dissolved in the waters of Lake Lahontan are buried. As between Lake Bonneville, another ancient lake of the Great Basin, and Lake Lahontan, the latter was chosen as the site of drilling operations for the reason that it never overflowed its banks and because its water drained an area where volcanic rocks predominated. It is in such rocks, as contrasted with sedimentary rocks, that appreciable quantities of potash and soda are contained. The headwaters of Lake Bonneville, on the other hand, were located in the Wasatch Mountains, where limestone occur and where potash and soda compounds therefore are present in comparatively small quantity.

A consideration of the low points in the Lahontan basin narrowed the selection of a drill site to a few localities, and the one chosen finally is in Sec. 30, T. 21 N., R. 30 E., at the north end of Timber Lake. The well is known as the Timber Lake well. In the publication by Gale cited above a summary of progress is given in considerable detail and shows the character of the rocks passed through. The well at the time the report was closed (Dec. 1, 1911) had reached a depth of 360 feet, but saline material had not been encountered in any appreciable quantity. It is expected that drilling will be continued until a depth of at least 1,000 ft. is reached.

POTASH SALTS IN BRINES AND BITTERNS.

In a previous publication of the United States Geological Survey¹ it was stated in general, with reference to the possible occurrence of potash salts in the United States, that to make a thorough and complete investigation of their occurrence, every known rock salt deposit should be closely watched, studied and tested from time to time. The reason for this statement lies in the fact that ordinary rock salt may both overlie and underlie deposits of potash salts. Both these conditions exist in the Stassfurt-Egeln district of Germany. The normal occurrence of rock salt is, however, at or

toward the base of a series of soluble salines deposited from the evaporation of sea water and hence below the potash salts. Too great emphasis can not be laid on the investigation of rock salt deposits for potash salts.

Private enterprise can and probably will go far in carrying on the investigation of the problem of a cheap and easily available supply of potash salts within the territory of the United States. The United States Geological Survey is ready and willing, so far as its limited means and equipment allow, to aid in this work, and already hundreds of inquiries have been answered and specimens examined in its offices and laboratories in Washington. All that can be done with most of the material received is to subject it to qualitative tests to determine the presence of soluble saline material. Such simple tests are, however, all that is necessary to determine the presence of soluble potash salts.

By a recent arrangement a co-operative laboratory has been established at the Mackay School of Mines, University of Nevada, at Reno, in which the University of Nevada, the Bureau of Soils of the United States Department of Agriculture, and the United States Geological Survey have combined in the interest of the potash investigations. This laboratory is under the administrative charge of Prof. George J. Young, at the Mackay School of Mines. Hereafter communications relating to such potash tests and samples for analysis may be directed to Prof. Young. Such tests as are deemed warranted will be made on the samples, subject to the limitations of equipment and capacity of the laboratory. A few requests have been received for the determination of supposed nitrate and phosphate samples. There is no provision in the equipment of the laboratory at Fallon for these tests, but it is expected that the Reno laboratory will be able to handle a reasonable amount of that work also.²

As a part of the potash investigation carried on by the survey in the summer of 1911, a systematic and fairly complete study of the brines, bitterns, and rock salt deposits of the states east of the Rocky Mountains was attempted. The study was confined to the localities that were considered the most promising for the occurrence of potash salts. During the work 175 samples of brines, bitterns, and calcium chloride were collected. This does not include the large number of brine samples procured through correspondence, chiefly from oil drillers throughout the country, earlier in the year. The geology of the occurrences of the brine and the salt was investigated and many records of deep wells were obtained. Where possible, actual samples of the rocks passed through in making the deep drillings were collected. Because so few of the samples (less than 25) collected or received by the survey have been reported on, a general statement of results at this time is impossible; but by reference to

¹Phalen, W. C., Occurrence of potash salts in the Bitterns of the eastern United States: Bull. U. S. Geol. Survey No. 530-B, 1911, 19 pp.

²Bull. U. S. Geol. Survey 530-A, 1911, p. 21. See also press notice dated Feb. 17, 1912, U. S. Dept. Agr.

the analyses given below it will be seen that many bitterns supposed to be devoid of potash salts do in fact contain them in small amounts. Particular attention is called to a natural bittern from northern Ohio which is known to occur over a large area and which in its content of potash salts stands out from the rest.

Analyses of the Brine.—The samples whose analyses are given in Tables I and II represent only a very small part of those submitted for examination. The care with which the work is being done requires a great deal of time, consequently the work has to proceed slowly. The chemical work thus far has been done by R. F. Gardner and A. R. Merz of the Bureau of Soils, Department of Agriculture.

COMPOSITION OF NATURAL BITTERN FROM FAIRPORT HARBOR, OHIO.

	Grams per liter.
Potassium chloride.....	7.4
Sodium chloride.....	110.1
Calcium chloride.....	134.4
Magnesium chloride.....	43.2
Calcium sulphate.....	.3
Ferric chloride.....	.3
Total	295.7

ALUNITE AS A SOURCE OF POTASH SALTS.¹

A deposit of alunite recently discovered near Marysville, Piute County, Utah, is being developed and may produce potassium sulphate on a commercial scale. The deposit is located near the head of Little Cottonwood Canyon about 7 miles southwest of Marysville,

TABLE I.—COMPOSITION OF CERTAIN OHIO BITTERNS.

Constituents, in grams per liter.

Sample No.	Source.	Description of sample.	K.	Na.	Ca.	Mg.	Cl.	SO ₄ .	Br.	Total.	Percentage Content of KCl.	Percentage KCl in total solids.
112	Union Salt Co., Cleveland.	Bittern from grainer 5 days old.	1.2	100.1	16.3	3.7	194.5	0.7	..	316.5	2.29	0.7
117	Ohio Salt Co., Wadsworth.	Bittern accumulating 35 days.	7	103.7	16.5	1.3	192.3	1.1	..	315.6	1.33	.4
118	do.	More concentrated bittern than No. 117; vacuum pan at boot.	1.8	97.6	12.0	2.4	187.8	1.8	..	303.4	3.43	1.1
114	Diamond Alkali Co., Fairport Harbor.	Natural bittern.	3.9	43.4	48.6	11.2	188.4	.2	..	295.7	7.43	2.5
122	Pomeroy Salt Association, Pomeroy.	Bittern before passing to bromine plant.	3.2	2.6	145.2	42.2	360.4	5.2	11.6	570.4	6.10	1.1

Of the analyses of bitterns given, that of sample No. 114 from Ohio deserves more than passing notice. It was collected at the plant of the Diamond Alkali Co. at Fairport Harbor, northeast of Cleveland, on Lake Erie, from a well during the process of sinking. Samples of similar natural bitterns were procured near Akron and also at Barberton. The top of this bittern stratum varies from approximately 350 to more than 400 ft. above the topmost salt bed from which artificial brines are pumped in northern Ohio. One record collected shows a difference of only 250 ft., but this seems very exceptional. It will be sufficient to state here that the bittern stratum is sharply defined and is of wide areal extent. The bittern is a bugbear to the salt industries of this part of Ohio, for if allowed to get into the brines from which salt is made it renders them bitter and as a consequence spoils the resulting salt. As a container of potash salts, this bittern may prove to be one of the richest known in the Eastern States.

A bittern of this composition seems to offer opportunities for research which should not be neglected.

On reducing the different constituents of this bittern from their ionic state to conventional combinations, the total solids would be divided as follows:

which is the present terminus of the San Pete & Sevier branch of the Denver & Rio Grande Railroad. It occurs high in the Tushar Range, at an elevation of 9,900 to 11,000 feet above sea level, or about 4,000 feet above the railroad at Marysville station.

The mineral alunite is a hydrous sulphate of potassium and aluminum with the symbol $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$. Theoretically it contains 11.4 per cent K_2O , 37 per cent Al_2O_3 , 38.6 per cent SO_3 , and 13 per cent water. The composition of the Marysville mineral, according to the analyses that follow, is very close to the composition of the pure mineral given above.

ANALYSES OF ALUNITE FROM DEPOSIT NEAR MARYSVILLE, UTAH.

	18.	19.	Dana.
	Per cent.	Per cent.	Per cent.
Al ₂ O ₃	37.18	34.40	37.0
Fe ₂ O ₃	Trace	Trace	..
SO ₃	38.34	36.54	38.6
P ₂ O ₅	.58	.50	..
K ₂ O	10.46	9.71	11.4
Na ₂ O	.33	.56	..
H ₂ O+	12.90	13.08	13.0
H ₂ O—	.09	.11	..
SiO ₂	.22	5.28	..
Total	100.10	100.18	100.0

¹Butler, B. S., and Gale, H. S., Alunite, a newly discovered deposit near Marysville, Utah; Bull. U. S. Geol. Survey No. 511, 1912, 64 pp.

TABLE II.—COMPOSITION OF CERTAIN WEST VIRGINIA BITTERNS.

Constituents, in grams per liter.

Sample No.	Source.	Description of sample.	K.	Na.	Ca.	Mg.	Cl.	SO ₄ .	Br.	Total.	Percentage Content of KCl.	Percentage KCl in total solids.
120	Dixie Salt Co., Mason.	Bittern from grainer before passing to bromine plant.	..	3.3	135.8	48.4	366.2	4.8	11.0	569.5	..	..
129	Liverpool Salt and Coal Co., Hartford.	Bittern before passing to bromine plant.	..	.2	143.4	43.4	358.6	3.8	12.2	561.6	..	..

No. 18 is a selected specimen of the supposedly best material. It consists of clear pink, subtransparent, coarsely granular crystalline rock. No. 19 is a selected specimen of a light pink, very finely granular rock, of almost porcelain-like conchoidal fracture and no distinct structure.

As yet the developments on the Marysvale properties have shown only what is thought to represent a single large vein of alunite.

A conservative estimate of the tonnage in this deposit may be had by assuming an average width of 10 ft. in the principal vein for a total length of 3,500 ft. and neglecting the rest of the deposit as not sufficiently proved to be taken into consideration at present. This gives a surface area of substantially proved outcrop of 35,000 sq. ft., or more than four-fifths of an acre. The specific gravity of the Marysvale alunite has been determined in several specimens by W. T. Schaller, with results in close accord at about 2.82. Therefore a cubic foot of the ore may be assumed to weigh about 175 lbs. An acre of ground underlain by this rock to a depth of only 1 foot would contain 3,800 short tons of alunite. If the area of available alunite is only 35,000 sq. ft., as stated above, there would be approximately 300,000 short tons of the rock for each 100 ft. of depth so long as the deposit maintains its surface dimensions and quality. If the recoverable potassa or potash (as K_2O) is estimated at 10 per cent of this total, such a deposit would yield 30,000 tons of potassa for each 100 ft. in depth. This is approximately one-sixth to one-seventh of the total annual consumption of potash in the United States.

The Marysvale deposit, so far as known, is not of such magnitude as to afford a source of all the potash salts now consumed in the United States, but it may prove to be an important factor in providing an American supply that will perhaps be especially available to local and western markets, particularly in meeting the demand for higher grade salts. Possibly also the greatest importance of the commercial development of this deposit will be in the added stimulus it may afford to exploration for other similar deposits of this mineral, especially in this general region, and it is on the discovery of such other deposits that the provision of a home supply from this source must depend.

Experiments by W. T. Schaller in the laboratory of the Geological Survey have showed that on igniting the powdered alunite all the water and three-fourths of the sulphuric acid are driven off. When the residue is leached with water potassium sulphate dissolves and insoluble alumina is left. The average amount of potassium sulphate leached from the ignited mineral is 17.9 per cent of the original material used. As the coarsely crystallized alunite was found to contain 19.4 per cent potassium sulphate, 92 per cent of the total potash present was obtained by simple ignition and subsequent leaching. According to the laboratory experiments 32.7 per cent of the ignited alunite consists of available potassium sulphate which may be obtained

by leaching and evaporation; the remaining 67.3 per cent is nearly pure alumina.¹

Several foreign deposits of alunite have been successfully worked for the manufacture of alum. The Utah mineral may be used for alum, or, as suggested by the laboratory work of W. T. Schaller, as a source of potassium sulphate and alumina.

Potash is abundant as a constituent of the rocks which form the crust of the earth. According to F. W. Clarke the percentage of potash (K_2O) in the earth's crust is 2.99, this result being an average of 1,488 determinations made in the laboratories of the United States Geological Survey up to November 1, 1910. In some varieties of igneous rocks, particularly those rich in the potash feldspars, there is a large amount of potentially valuable potash. The feldspars are widely distributed minerals and comprise about 60 per cent of the igneous rocks. Among the igneous rocks containing large amounts of potash are the glasses, of which the chief are obsidian, pumice, perlite and pitchstone. In these rocks the potash may run as high as 5 or 6 per cent. The rhyolites are also rich in potash. Examples of this rock containing more than 5 per cent of potash are common, and a certain rhyolite from Silver Cliff, Colo., has been shown to contain 8.38 per cent.²

The trachytes and phonolites are also rich in potash, as they consist chiefly of that variety of potash feldspar (orthoclase) known as sanidine. Some of the trachytes are known to contain nearly 8 per cent of potash. Among the granitoid rocks should be mentioned granite, monzonite and syenite, which contain considerable amounts of the potash feldspars. The leucite rocks of the Leucite Hills, Wyoming, contain, so far as known, the largest amount of potash among the igneous rocks. In many localities there occur large dikes or deposits of more or less pure feldspar, commonly orthoclase, which run much higher in potash than the ordinary granitic rocks and may contain nearly the theoretical potash content of pure orthoclase feldspar—16.8 per cent of potash. Such deposits have been developed in the New England states, Pennsylvania, New York, and Maryland, where they have been mined extensively and the feldspar has been ground to fine powder, principally for use in pottery manufacture.

But the potash of these rocks, even when finely ground, is tightly locked up, being practically insoluble by any known cheap commercial process. Rock bearing 10, 8, or even 6 per cent of potash—and there are millions of tons of such rock well distributed over the globe—would be highly valuable as a fertilizer were there any known cheap method of making the potash available for immediate use to the growing plant.

POTASH-BEARING ROCKS OF THE LEUCITE HILLS, WYOMING.¹

In connection with the problem of the extraction of potash salts in soluble form from the igneous rocks a source of supply of the latter, rich in potash salts, becomes a matter of interest. The igneous rocks, as

¹The data of geochemistry, 2d ed.: Bull. U. S. Geol. Survey No. 491, 1911, p. 27.

²Cross, Whitman, Proc. Colorado Sci. Soc., Dec. 5, 1887, p. 229.

stated above, are very widespread. They are, however, made up largely of quartz and other nonpotash-bearing minerals. Their potash content varies considerably but is always low. One of the richest potash-bearing rocks known in the United States is found in the Leucite Hills, Wyoming. Objection has been raised to this rock as a source of potash, owing to its remote location from the chief centers of consumption. It is true that the Leucite Hills are located remotely from the southern Atlantic States, which are at the present time the great consumers of artificial fertilizers. It will be, however, only a short time before certain of the Middle and Western States must use artificial fertilizers, and in some of them such use has already begun. This objection, therefore, to the Wyoming material can not be regarded as wholly valid.

The Leucite Hills are located in the north half of the Rock Springs dome, Sweetwater County, Wyo. The Union Pacific Railroad is the only line crossing this area, and spur tracks would have to be constructed from its main line along the larger valleys or main streams to tap the leucite-bearing area.

The potash contained in the leucite-bearing rocks occurs in the minerals leucite, phlogopite, one of the micas, sanidine, the glassy variety of orthoclase, glass, and to a small degree in diopside. The greater part of the potash occurs in the first two minerals named. The chemical analyses of the leucite-bearing rock samples show that their potash content ranges from 7.99 per cent to 11.91 per cent, averaging for nine analyses 10.74 per cent and for the eight samples of wyomingite and orendite, the igneous rocks containing the largest amount of potash, 11.08 per cent. Taking 10 per cent as a moderate average of the content of potash there are stored in the lavas in the Leucite Hills the amounts of leucite-bearing rock and potash indicated in Table III.

TABLE III.—SUMMARY OF THE AVAILABLE LEUCITE-BEARING ROCK AND POTASH FROM THE SEVERAL EXPOSURES OF THE LEUCITE HILLS, WYOMING.

	Leucite-bearing rock, in short tons.	Potash (K ₂ O), short tons.
Badger Teeth.....	17,841,105	1,784,110
Black Rock Mesa.....	157,237,200	15,723,720
Boars Tusk.....	28,994,384	2,899,438
Cross Mesa.....	78,732,540	7,873,254
Emmons Mesa.....	94,630,000	9,463,000
Endlich Hill.....	206,584	20,658
Hague Hill.....	376,712	37,671
Hallock Butte.....	11,450,970	1,145,097
Hatcher Mesa.....	5,127,300	512,730
Iddings Butte.....	11,526,932	1,152,693
Matthew Mesa.....	17,519,690	1,751,969
North Table Mesa.....	15,192,000	1,519,200
Orenda Mesa.....	149,976,184	14,997,618
Osborn Mesa.....	5,697,000	569,700
Pilot Butte.....	6,080,000	608,000
South Table Mesa.....	108,774,720	10,877,472
Steamboat Mountain.....	206,181,800	20,618,180
Table Mountain.....	4,177,800	417,780
Weed Butte.....	11,431,980	1,143,198
Zirkel Mesa.....	1,042,341,276	104,234,127
Total	1,973,496,177	197,349,617

¹Schultz, A. R., and Cross, Whitman. Potash-bearing rocks of the Leucite Hills, Wyoming: Bull. U. S. Geol. Survey No. 512, 1912, 39 pp.

²Bull. U. S. Geol. Survey No. 512, 1912, pp. 35-36.

These figures do not take into consideration the rock that occurs in the dikes associated with the volcanic necks and surface flows, nor the material underlying the mesas which has not been estimated in the discussion of the separate exposures. If the volcanic cones on Emmons, Zirkel, and Orenda mesas and Steamboat mountain represent volcanic conduits or necks similar to the volcanic necks seen at Boars Tusk, Badger Teeth, and Iddings Butte, there is considerable leucite-bearing rock in these localities that has not been included in the estimate. Some idea of the amount of material below the mesa for each conduit may be obtained by comparison with the amount estimated for the portions of the Boars Tusk and Badger Teeth lying below the level of the valley.

The figures in the above table for Pilot Butte are based on a 10 per cent potash content, the amount assumed for all the other localities, where as in the computations used in the discussion under the heading of Pilot Butte, 8 per cent potash, the result as determined by one analysis of this rock, was used.

THE CHEMICAL MANUFACTURERS IN THE UNITED STATES DEPENDENT ON IMPORTED POTASH SALTS.

The chemical industries in the United States dependent on potash salts are of enormous magnitude. A list of these industries has already been given on pages 25-26, under "Applications." Further details relating to these industries are given in the following pages, together with the statistics of their production, wherever it was possible to obtain them.

Potash.—Under the head of potash are included potassium carbonate and caustic potash. The former was for a long time the best known potash salt, being the residue from boiling lye from wood ashes in iron pots, whence the name potash. Potassium carbonate is now almost entirely made from potassium chloride by the LeBlanc process, in the same way as soda ash from salt, but the ammonia process can not be employed, because the acid carbonate of potassium (KHCO₃) is soluble in ammoniacal solutions and does not precipitate. The material is sold in the trade under the name potash or pearlash and is used chiefly in the glass industry, in the manufacture of caustic potash, and in the manufacture of chromates of potassium. A considerable quantity is bought by soap makers and causticized, the solution being used for soft soaps.

Caustic potash (KOH) is made in a similar manner to caustic soda. It is much more deliquescent than the corresponding sodium compound and is generally made where it is to be used. In soap making it was formerly customary to saponify the fat with caustic potash and then add common salt. An interchange between the potassium and sodium took place, the result being a hard sodium soap. But as soda is now cheaper than potash and yields a hard soap directly, potash soaps are used only for special purposes. The magnitude of the industries using this class of potash salts may be judged by the importations given in the table on a preceding page.

Alums.—In the manufacture of potash alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$) large quantities of potassium sulphate are used. On the addition of the potassium sulphate to the sulphate of alumina the potash alum crystallizes out in extremely pure form. Alum is extensively used in the dyeing industry as a mordant and by paper makers and leather dressers. It is also used in making pigment lakes, clarifying turbid liquids, and precipitating sewage, and for hardening plaster of Paris casts, etc. A small quantity is used in medicine. The following table gives the quantity and value of potash alum manufactured in the United States at the censuses of 1899, 1904, and 1909:

POTASH ALUM MANUFACTURED IN THE UNITED STATES, 1899, 1904, AND 1909.		
	Quantity, Pounds.	Value.
1889	11,200,393	\$215,004
1904	10,307,154	156,448
1909	10,253,802	155,319

Cyanides and derived compounds.—The class of cyanides comprises potassium cyanide; sodium cyanide and other simple cyanides, includes "cyan-salt," a mixture of potassium and sodium cyanides; potassium ferrocyanide (yellow prussiate of potash); potassium ferricyanide (red prussiate of potash). There are also the cyanates and ammonium and potassium sulphocyanates, etc.

forming aurous potassium cyanide ($AuCN \cdot KCN$). It was formerly used in photography for "fixing" the image, but for this purpose it has been largely replaced by sodium thiosulphate.

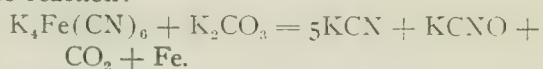
Potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$), also called yellow prussiate of potash, is made by fusing together potassium carbonate, iron borings, and nitrogenous organic matter of any kind, such as horn, hair, blood, wool waste, and leather scraps. The material in its pure form is produced in splendid large lemon-yellow crystals. It is not poisonous. It is largely used for making Prussian blue; in calico printing and in dyeing; for case-hardening iron; for making potassium cyanide and ferricyanide; and to a small extent in explosives and as a chemical reagent.

Potassium ferricyanide, or red prussiate of potash (K_3FeCN_6), is usually made by passing chlorine gas into a solution of the ferrocyanide until ferric chloride no longer forms a precipitate, but produces only a brown color in the liquid. It may also be made by exposing the dry powdered ferrocyanide to chlorine until a test portion dissolved in water gives nothing but a brown color, with ferric chloride. With ferrous salts, it gives the blue pigment Turnbull's blue. Its solution with caustic potash is a powerful oxidizing liquid and as such is used in calico printing for a "discharge" on

TABLE IV.—CYANIDES MANUFACTURED IN THE UNITED STATES, 1899, 1904, 1909.

	1899.	1904.	Increase—		Percentage of Increase—	
			1899.	1899 to 1904.	1899	1904
Quantity, pounds	8,460,989	11,196,318	13,291,080	2,735,329	32.3	18.7
Value	\$1,595,505	\$1,710,823	\$1,941,893	\$115,318	7.2	13.5
Value per pound.....	\$0.189	\$0.153	\$0.146			

Potassium cyanide (KCN) is generally made by fusing potassium ferrocyanide with potassium carbonate until the evolution of gas ceases. The following is the reaction:



The metallic iron that is produced sinks to the bottom of the crucible, and the fused mixture of cyanide and cyanate is run off. The addition of powdered charcoal reduces part of the cyanate to cyanide. The product thus prepared is pure enough for many purposes. The commercial salt always contains cyanate and carbonate and is sold in various grades, depending on the purpose for which it is to be used. The best quality contains about 98 to 99 per cent KCN, but ordinary grades contain only 65 to 70 per cent. It is a very powerful reducing material when heated with reducible substances, and hence its use as a flux. It is extremely poisonous, either when taken internally or when introduced directly into the blood. It is extensively employed in electroplating as the solvent in the bath, forming soluble double cyanides with gold, silver, copper and other metals. It is also used as a flux in assaying and metallurgy. Its greatest use at the present time is for the recovery of gold from low grade ores and the tailings of other reduction processes. A weak solution is used to dissolve the gold,

indigo and other dyes. It also forms part of the sensitive coating of blueprint papers. It has been recommended for use with potassium cyanide solution in gold extraction.

Table IV shows the magnitude of the cyanide industry in the United States at the censuses of 1899, 1904 and 1909.

Fertilizers.—The fertilizers comprise numerous chemical compounds, among them the so-called complete fertilizers, which consist of superphosphate of lime, potash salts, and ammoniacal or other nitrogenous compounds, including nitrates. Table V gives the quantity and value of complete fertilizers manufactured in the United States at the censuses of 1899, 1904, and 1909, together with the amount and percentage of increase. The increase both in quantity and in value in the last census is very large:

Table VI gives the quantity and value of the principal potash materials used in fertilizers in the United States at the three censuses cited, with the amount and percentage of increase. This table includes only the materials used in the principal establishments in the United States. The increase in the amount and value of kainite and potash salts used in the manufacture of fertilizers in 1909 as compared with 1904 is very notable.

Bleaching materials.—The class of bleaching ma-

terials includes, among a great many other chemicals, potassium bisulphite. Potassium bisulphite forms a very small part of the total. Table VII gives the quantity and value of bisulphites manufactured in the United States at the censuses of 1899, 1904, and 1909, with the amount and percentage of increase:

TABLE V.—COMPLETE FERTILIZERS MANUFACTURED IN THE UNITED STATES, 1899, 1904, 1909.

	1899.	1904.	1909.	Increase		Percentage of Increase	
				1899 to 1904.	1904 to 1909.	1899 to 1904.	1904 to 1909.
Quantity, short tons.....	1,478,826	1,603,847	2,949,083	125,021	1,345,236	8.4	83.9
Value	\$26,318,995	\$31,305,057	\$62,050,731	\$4,986,062	\$30,745,674	18.9	98.2

Potash salts consumed in manufacture of electrochemicals.—The figures given in Table VIII for potash salts in 1899 and 1904 are for the quantity and cost of potassium salts consumed as material in the manufacture of electrochemicals and not for the potash salts made electrolytically. Statistics are not available for the electrolytic production or for the quantity

platives industry in the United States in the years 1899 and 1904, the figures for 1910 not being available:

POTASSIUM NITRATE USED IN THE MANUFACTURE OF EXPLOSIVES IN THE UNITED STATES, 1899 AND 1904.

1899		1904	
Quantity.	Value.	Quantity.	Value.
Short tons.		Short tons.	
3,315	\$270,186	4,114	\$308,644

TABLE VI.—PRINCIPAL POTASH MATERIALS USED IN FERTILIZERS IN THE UNITED STATES, 1899, 1904 AND 1909.

	1899.	1904.	1909.	Increase		Percentage of Increase	
				1899 to 1904.	1904 to 1909.	1899 to 1904.	1904 to 1909.
Kainite:							
Quantity, short tons.....	54,700	190,493	347,104	135,793	156,611	248.3	82.2
Value	\$520,833	\$1,891,070	\$3,008,183	\$1,370,237	\$1,117,113	263.1	59.1
Potash salts:							
Quantity, short tons.....		123,267	269,979		146,712		119.0
Value	\$3,130,556	\$3,645,740	\$7,708,542	\$515,184	\$4,062,802	16.4	111.4

^aIncludes nitrate of potash amounting to 1,160 tons, valued at \$39,039.

^bIncludes nitrate of potash to the value of \$32,156.

and cost of potash salts consumed as raw material in 1909.

TABLE VIII.—POTASH SALTS CONSUMED IN MANUFACTURE OF ELECTROCHEMICALS IN THE UNITED STATES, 1899 AND 1904.

	1899.	1904.	Percentage of increase.	
Quantity, short tons	1,900	3,908	2,008	105.7
Value	\$80,097	\$200,008	\$119,911	149.7

Dyestuffs.—Potash salts enter into the dyeing industry chiefly in the form of alum. The production of alum has already been given and will not be repeated here. Potassium sulphide is frequently used

General Chemicals.—Under the heading of general chemicals potash enters into the composition of a host of substances. Some of these are arsenite of potassium, used in the dyeing industry; bromide of potassium, used in photography and medicine; chlorate of potassium, used in fireworks, matches, and aniline colors; chromate of potassium, used in dyeing and electrical cells; manganate and permanganate of potassium, used in dyeing and bleaching, in disinfectants, and in medicine; silicate of potassium, used in making ordinary yellow soaps, as a fixative for pigments in

TABLE VII.—SODIUM, POTASSIUM, CALCIUM, AND OTHER BISULPHITES MANUFACTURED IN THE UNITED STATES, 1899, 1904, AND 1909.

	1899.	1904.	1909.	Increase		Percentage of Increase	
				1899 to 1904.	1904 to 1909.	1899 to 1904.	1904 to 1909.
Quantity, short tons.....	1,461	6,223	8,119	4,762	1,896	325.9	30.5
Value	\$34,486	\$110,155	\$445,371	\$75,669	\$335,216	219.4	304.3

to improve the "fire" in vermilion. Potassium bichromate is extensively used in the manufacture of chrome green.

Explosives.—Potash salts in the form nitrate enter into the manufacture of gunpowder. The term "gunpowder" generally includes the nitrate-sulphur-charcoal combination used in blasting as well as that used in guns, and for the last 50 years it has included the blasting powder made with nitrate of soda as well as that made with nitrate of potash. Potassium nitrate is also a constituent of some of the higher grade explosives tested and listed by the Bureau of Mines as

calico printing, as a vehicle for pigments in fresco painting, for rendering cloth and paper noninflammable, etc.; cream of tartar; and argols.

The Australian Journal of Pharmacy states that large quantities of eucalyptus oil are being consumed in the Australian mining districts in the processes of preparing sulphides of zinc and lead. According to this Journal about 1 lb. of oil is emulsified by vigorously shaking it up with 100 gals. of water, and with this mixture the moistened or powdered ore is stirred up.

THE LABORATORY

THE LABORATORY OF ORGANIC CHEMISTRY AT THE ARMOUR INSTITUTE OF TECHNOLOGY.

By B. B. FREUD.

The laboratory for organic chemistry at the Armour Institute of Technology embodies some new ideas in laboratory construction that make it worthy of being described in the literature. The laboratory has been in service for a school year, insuring a thorough test of the new features. These have given entire satisfaction, except in certain details which will be noted later. And for the reason it is deemed desirable to describe the whole laboratory in detail.

The primary object was to approach as nearly as possible to an absolutely fireproof construction. The



Fig. 1—View of Locker.

room selected for the laboratory is on the third floor of the main building in the southwest corner, 20 ft. on the south, 37 ft. on the west and 16 ft. high. The south and west walls are the brick walls of the building. The north and east walls are of hollow tile construction. The floor is of cement laid on cinders. The ceiling is of hard wood beam construction, which it was not found possible to change. It was decided to make the lockers of sheet iron, with soap stone tops. The only wood in the room is the window mill work and the ceiling.

The second object was to accommodate as many students at one time as was possible, and at the same time give each student sufficient room to carry on several preparations simultaneously. The great problem in a course of this kind is to provide sufficient table surface. The locker space usually takes care of itself. The laboratory was designed to accommodate 24 students. The plan of the arrangement is given in

Fig. 3. At one time it was thought desirable to have a community arrangement: A distillation rack with the condensers already set up; evaporating tables, one a water bath, another a hot plate, etc. This idea was finally abandoned as not being adaptable to the conditions at hand. But it is mentioned here because in



Fig. 2—View of Laboratory.

our opinion it could be developed successfully, saving space and also much of the students' time.

It will be noted that there are two large sinks, one in the southeast corner, the other diagonally opposite. These are provided with hot and cold water. They are to be used exclusively for cleaning apparatus. This permits the elimination of the long trough that usually runs through the center of laboratory tables, and instead it permits the use of small individual sinks distributed at appropriate places in the tables. These are to be used merely for carrying off condenser water and spent liquid reagents. They are

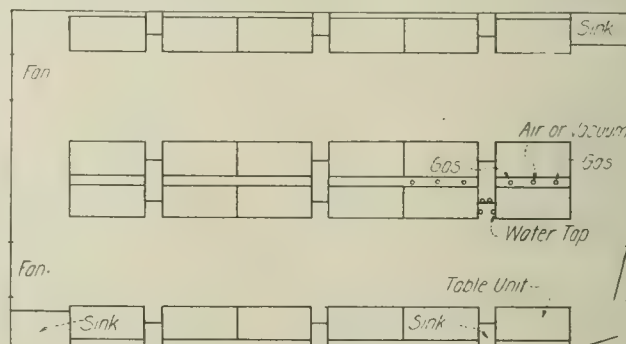


Fig. 3—Arrangement of Laboratory.

also designed so they can be used as pneumatic troughs.

There are four tables arranged as shown in Fig. 3, the east and west tables being single and the center one double. The table tops are of soap stone, laid

on top of the sheet iron tops of the table units. It would have been better had the table units been made without tops. The soap stone covering is more than able to support itself and its load. Much difficulty in leveling would thus have been avoided.

Each table is made up of six locker units separated by a 1 ft. space. The table top, however, covers this space, except for the space occupied by the sinks. The space between the lockers and under the sinks is used for the solid refuse jars, thus keeping the aisles clear. The soap stone top extends 3 in. over the back of the single tables, and there is a 6 in. space between the sections of the double table over which the soap

particular, thus reducing the manufacturing cost. To each student is assigned one unit, consisting of four drawers, and a large locker compartment. These five spaces are locked by a large plate and one lock. The student has a working surface of 5 ft. by $2\frac{1}{4}$ ft. He shares with one other student a table sink. He has for his own use one water tap running into the table sink and a T tap running from it from below the faucet. This is to lead into the condenser. Thus he has two water taps from one pipe line. He has three gas taps, one air pressure tap, and one vacuum tap. All these are nickel plated. This has stood up fairly well, and with occasional polishing does not cor-

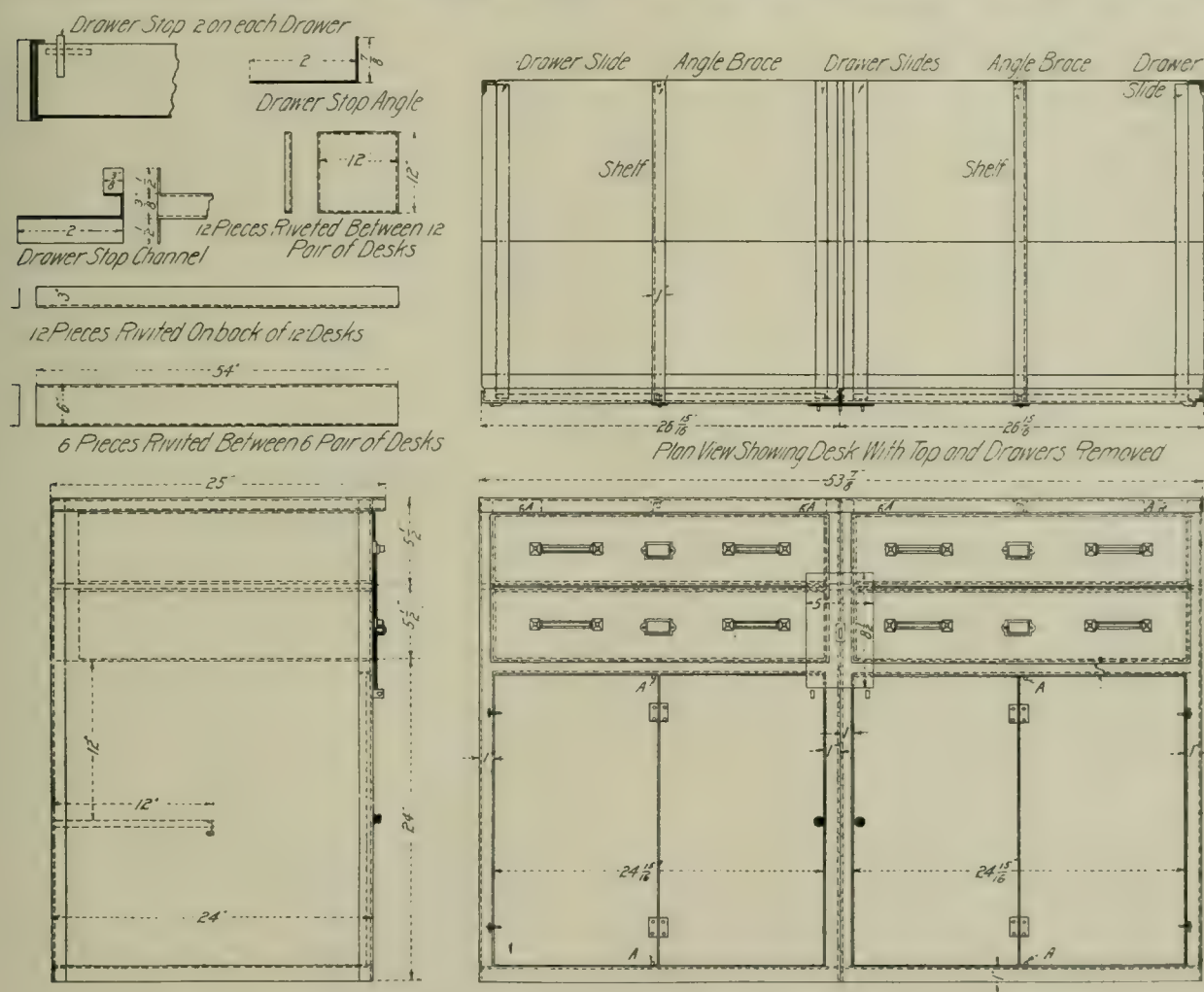


Fig. 4—Details of Locker Units in Laboratory of Organic Chemistry, Armour Institute.

stone top extends. Under this are the drain, water, compressed air, vacuum and gas pipes. All plumbing and fittings are outside the locker units. This makes renewal of parts and repairs easy. There are no shelves or fittings above the soap stone, except the water taps and gas cocks, thus giving an unrestricted use of the table top for the apparatus.

The locker units are shown in detail in Fig. 4. They are of sheet steel, protected with two coats of liquid carbon paint. They were made after our own design by the Durand Steel Locker Co. In order to facilitate handling they were made in 24 small units, each one a complete locker. They are exactly alike in every

rode as much as might be expected. These fittings are the only things that rise above the table tops.

We plan to have electrical connections to the 110 volt line and to a battery of 45 lead storage cells, thus permitting us to apply electro chemical methods to preparations, particularly to use the important oxidation and reduction methods.

In planning for the hoods it was found that adequate provision could not be made without lowering very considerably the student capacity of the laboratory. In order to save the space that would thus be required, the whole laboratory is treated as one large hood. In the south wall, about two-thirds up from

the floor are two Sturtevant fans connected with rheostats and individually controlled. When both are operated at maximum speed the movement of the air is too great. Under these circumstances the burner flames must be shielded. By proper regulation of the speed the ventilation can be adjusted to the needs of the immediate occasion. There is a hood in an adjacent laboratory in which such substances as bromine, fuming nitric acid and phosphorous penta chloride can be transferred.

The laboratory is directly connected with the supply room by means of a serving window in the north wall. Students in organic chemistry require much more supply room service than students in any other courses, for that reason the laboratory was located as near the storeroom as was possible.

On the whole the laboratory has given excellent satisfaction. And it reduces the fire hazard to a minimum. So far as we know it is the only laboratory which has attempted to use steel in the locker construction. Longer time will be necessary before final judgment is passed on such construction.

The principal gold mines of the Black Hills, according to Charles W. Henderson, of the United States Geological Survey, were steadily operated in 1911, and a heavily increased yield, only slightly below that of the record year, 1908, was the result. The Homestake mine, which produces each year the bulk of the gold bullion from this state, at the beginning of the year had completely overcome the labor difficulties of 1909-10 and was again operating at the full capacity of its plant of 1,000 stamps with cyanide, sand, and slime plants. The other large properties were correspondingly active. Of particular interest in the northern Black Hills are the progress on the hydraulic-electric plant of the Homestake Co.; the building at Galena of the new Osterman-Danckwardt pyritic smelter, and of the Gilt Edge Maid concentrating plant; the proposed increase in the capacity of the Golden Reward cyanide plant by the addition of a roaster; the open-cut mining and low costs of the Wasp No. 2 Co.; the building of the 300-ton cyanide plant of the Bismarck Co.; and the testing of the deposits of zinc ore near Deadwood. The operation for 5½ months of the first dredge in the Black Hills, at Mystic, Pennington County, and of several properties near Hill City, Keystone, and Oreville were the principal features of interest to the mining industry in the southern Black Hills. According to preliminary figures compiled by the Director of the Mint, South Dakota produced in 1911 \$7,430,367 in gold and 206,188 ounces of silver, valued at \$113,403, against \$5,380,200 in gold and 120,600 ounces of silver, valued at \$65,100, in 1910.

The French Official Gazette publishes the law authorizing the Paris municipality to raise a loan of \$40,000,000 for improving the gas service of the city.

SOME METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

The value of an analysis for technical purposes depends upon the fulfillment of two equally important conditions: First, a sample must be prepared which is truly representative of the entire mass of material, and after that the sample must be carefully and intelligently analyzed by a sound method. The most perfect analysis of a non-representative sample is as valueless as a bad analysis.

In the methods to be described, it is assumed that the material under discussion has been properly sampled and prepared for analysis.

In general, the analysis for technical purposes does not demand the highest scientific accuracy. Also, the technical laboratory must turn out work, as a rule, more rapidly than the greatest accuracy of method would allow.

There is little originality in the methods to be described here. They are all founded upon well known and established principles, and are similar to those given in the best literature of analytical chemistry. They represent, in each case, careful selection and adoption from standard methods, made with a view to convenience of manipulation and as much speed as is consistent with accuracy.

THE ANALYSIS OF LIMESTONE.

The substances ordinarily determined are the following:

SiO₂ (and insoluble matter)
Fe₂O₃
Al₂O₃ (+Mn₂O₄)
CaO
MgO
CO₂
SO₃
Loss on ignition.

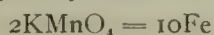
Silica and Insoluble Matter.—The 1 gram sample in a small casserole is moistened thoroughly with 10 c.c. of water and then decomposed by the addition of 5 to 10 c.c. of HCl sp. gr. 1.2 and the whole evaporated to dryness over boiling water or on the 100° electric hot plate. The dry residue is drenched with concentrated HCl, taken up with the least amount of hot water, and the whole heated to the complete solution of everything soluble. It is then filtered, the residue washed once with hot water and the solution re-evaporated at 100° C. and dehydrated one hour at 120° C. The dry residue is again taken up in HCl and hot water, boiled and filtered through the same paper as before. The residue is washed 4 or 5 times, the paper burned wet in a platinum crucible, heated for five minutes over the blast lamp or Meeker burner, cooled and weighed as "SiO₂ + insoluble matter," the insoluble matter being, for the most part, silicates undecomposed by HCl.

Ferric and Aluminum Oxides.—The filtrate from

the SiO_2 , etc., should be about 75 c.c. in bulk. To this a little bromine water is added to assure the oxidation of iron and manganese, and then NH_3 solution (sp. gr. 0.90) added to complete precipitation, plus an excess of about 5 c.c., the whole being boiled. The precipitate formed is redissolved by the cautious addition of HCl and then reprecipitated by dilute ammonia, a very slight excess being used. This treatment assures the presence of enough ammonium chloride to hold magnesium in solution. The solution is now boiled until the odor of MH_3 is barely perceptible, to insure complete precipitation of $\text{Al}(\text{OH})_3$, and filtered hot, the precipitate is immediately redissolved, into the original beaker by a stream of hot dil. HCl from the wash bottle, the paper washed clean, the FeAl (and Mn) reprecipitated by NH_4OH , the excess of NH_3 boiled off and the precipitate thrown upon the same filter as before. (It is well to first pour a few drops of NH_4OH on the filter to assure the absence of acid.) The paper is burned wet in platinum, ignited, blasted thoroughly and weighed as $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 (+\text{Mn}_2\text{O}_4)$.

When the Fe_2O_3 is desired, the ignited precipitate, after weighing, is fused with 1.5-2 grms. of KHSO_4 at a red heat, and the melt leached out with hot water and a little H_2SO_4 . This solution contains ferric and aluminum sulphates. It is transferred to an Erlenmeyer flask, 0.5 gm. of iron-free zinc (20-30 mesh) added and allowed to dissolve completely, and the iron titrated cold with MnOKMnO_4 . The weight of $\text{Fe} \times 1.4294 = \text{Fe}_2\text{O}_3$, and this subtracted from the weight of combined oxids gives the alumina. When duplicate samples are run, it is convenient to ignite and weigh one of them, and dissolve the other in hot dilute H_2SO_4 from a wash bottle, reduce the solution with zinc and titrate as before.

Determination of CaO .—The combined filtrates from the iron and alumina (about 150 c.c.) are heated and boiled throughout the addition of a hot solution of $(\text{MH}_4)_2\text{C}_2\text{O}_4$, plus a little ammonia, and the boiling continued five minutes, when the solution is transferred to the water bath for one hour. The CaC_2O_4 should settle readily and be retained by an ordinary filter paper. The filtered and washed CaC_2O_4 may be ignited to CaO over the blast lamp or Meker burner and weighed as such, but it is more convenient to treat it as follows: After thorough washing the bulk of the precipitate is washed into a 400 c.c. beaker by a stream from a wash bottle containing hot 10 per cent H_2SO_4 , the paper washed thoroughly with the same solution, the solution (made up to about 200 c.c. with water) boiled, and the liberated oxalic acid titrated hot with KMnO_4 . The titration should be slow, especially toward the end. Since



So, the Fe st d : the CaO st d : : 10 (55.9) : 5 (56). Ordinarily the CaO standard may be taken as twice the iron standard.

Determination of MgO .—While the CaO is being titrated the filtrate from the CaC_2O_4 is evaporating to 100-150 c.c. It is first just acidified with HCl and then NaNH_4PO_4 added in slight excess. While still warm, dilute MH_3 solution is added, with constant stirring. As soon as the precipitate of MgNH_4PO_4 appears, a 10 c.c. excess of concentrated ammonia is added, and the solution allowed to stand over night. This procedure should always give a beautifully crystalline precipitate. The precipitate is filtered off in the cold, washed with dilute NH_3 and dried in the air bath, when the filter paper with precipitate is transferred to a porcelain crucible, burned and ignited in a muffle until the precipitate is white. $\text{Mg}_2\text{P}_2\text{O}_7$ is weighed and MgO calculated. $\text{Mg}_2\text{P}_2\text{O}_7 \times .3624 = \text{MgO}$.

Frequently a gray color in the ignited precipitate persists even on long heating. The writer has found in many trials that he is unable to weigh the difference between the grayish precipitate and the same precipitate when finally burned white. A half hour's ignition in the muffle, after the paper is burned should be sufficient.

Loss on Ignition.—A sample of 0.5 gm. is heated first in the muffle and finally over the blast, to constant weight.

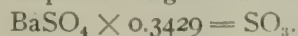
Carbondioxide Determination.—It is not often that a direct determination of CO_2 is demanded. Ordinarily, and particularly when iron is low, the CaO and MgO calculated to CaCO_3 and MgCO_3 gives a satisfactory result for CO_2 . The difference between the loss on ignition and the CO_2 so calculated gives organic matter and moisture.

The above described method is directly applicable to lime and lime products, and all similar bodies, and when accompanied by determinations of sulphur trioxide and free lime, to cements and cement rocks.

DETERMINATION OF SO_3 IN CEMENT.

In the analysis of cement it is well to use a larger sample, say 2.5 grams, decompose and dehydrate as described under the "Determination of Silica," take up in acid and water as usual and make up to 250 c.c. in a volumetric flask. Of this solution, 100 c.c., equivalent to 1 gram, is taken for the determinations of Fe_2O_3 , Al_2O_3 , CaO and MgO .

For SO_3 , a second portion of 100 c.c. is neutralized by ammonia, acidified with HCl , and treated with BaCl_2 in slight excess. The whole is allowed to stand several hours, preferably over night, the BaSO_4 filtered off, washed, the paper burned in platinum, and the ignited precipitate weighed as BaSO_4 .

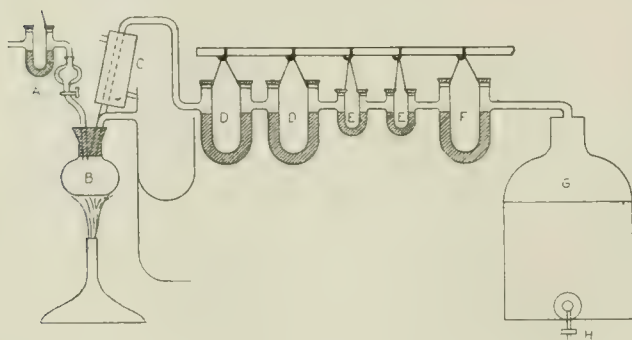


If SO_3 is to be determined upon a separate portion of cement, the 1 gram sample is decomposed with HCl , evaporated almost dry, taken up in water, filtered, and the filtrate, diluted to 150 to 220 c.c. precipitated as above by BaCl_2 . The presence of silicic acid in solution does not effect the determination (Hillebrand).

Determination of Free Lime in Cement.—A 1 gram sample is placed in a large beaker and about 250 c.c. of water added, the whole being thoroughly stirred and then allowed to stand 10 to 15 minutes. This hydrates and dissolves the uncombined lime. Two drops of phenolphthalein are added and the alkali titrated very slowly with N/10 HCl to the disappearance of the pink color. Volume of N/10 HCl $\times$ 0.0056 = weight of free CaO.

DIRECT METHOD FOR CO₂ IN CARBONATE ROCKS AND SIMILAR BODIES.

The apparatus shown below is convenient for this determination:



A contains soda lime.

B is the decomposition flask.

C a small water condenser.

D, a drying tube containing glass beads and concentrated H₂SO₄.

D contains fused CaCl₂ saturated with CO₂.

E E are glass stoppered V tubes containing fresh soda lime.

F is a guard tube, the left arm containing CaCl₂ and the right soda lime.

The large aspirator bottle provides for the drawing of air through the apparatus.

The 1 gram sample (larger if for small percentages of CO₂) is weighed out into B and covered with a little water, and then air is drawn through the apparatus by opening the cock at H, the tube A removing all CO₂ from the air. After five minutes the air is shut off, HCl (1:3) placed in the dropping funnel and the tubes E, E weighed and replaced.

Acid is then added very slowly, to the sample in B, the supply being so regulated as to permit not more than three bubbles per second to pass through D. When all action ceases, the solution in B is boiled gently, air being slowly drawn through the apparatus the while. The boiling is continued for about 10 minutes, then the flame removed and air drawn slowly through the apparatus for 20 minutes more, when the tubes E, E are removed, cooled in the balance case for 20 minutes and weighed. The increase in weight is the CO₂. If the substance for analysis contains sulphides, a tube containing a pumice and COSO₄ is placed ahead of the first drying tube D.

Water must flow through the condenser throughout the determination.

METHODS OF ANALYZING COAL AND COKE.

By FREDERIC M. STANTON and ARNO C. FIELDNER.

Several requests have recently been received for methods to be used in fuel analysis, we therefore publish these methods as the ones in use in the laboratories of the Bureau of Mines.

PRELIMINARY TREATMENT OF SAMPLES.

The coal samples are received at the laboratory in galvanized-iron cans that contain when full about 3 lbs. of coal. Each can has a close-fitting screw cap, and is made practically moisture-tight by a piece of electrician's tape wrapped around the joint between the cap and the top of the can. The method of collecting and shipping a sample is described in Technical Paper 1 of the Bureau of Mines.¹ Immediately after a sample is received at the laboratory, it is given a laboratory number, is removed from the can, and is placed in a weighed tin pan about 9½ ins. in diameter and 1¼ ins. deep. The tin pan containing the sample is placed in a large drying oven (Fig. 1), in which a temperature of 30° to 35° C. is maintained. Through this oven a current of warm air is drawn by means of an ordinary desk fan mounted on top of the oven.

The sample is dried under these conditions until the loss in weight between two successive weighings, made 6 to 12 hours apart, does not exceed 0.2 per cent. The purpose of this drying is to reduce the moisture in the sample to such a condition that rapid change in weight will not take place while the sample is being handled in the course of analysis.

The loss of weight by air drying is not regarded as an accurate determination, and the "air-drying loss" reported in an analysis simply means that the sample lost the stated percentage of moisture before it came to a condition of moisture equilibrium with the air of the room, at a temperature of 30° to 35°c.

After being air-dried in this oven, the sample is crushed to 10 mesh and finer, and quartered down to about 400 grams. This 400-gram portion is put in the porcelain jar of an Abbe ball-mill, sealed air-tight, and ground down to 60 mesh. The jar is about one-third full of well-rounded flint pebbles, 1 in. in diameter, and is rotated about 60 revolutions per minute. The 60-mesh sample is mixed thoroughly, and about 60 grams is taken for analysis. This 60-gram sample is kept in a rubber-stoppered, wide-mouthed bottle, which is numbered and dated.

METHODS OF ANALYSIS.

Moisture.—A 1-gram sample of the 60-mesh coal is placed in a weighed ⅞-in. by 1¼-in. porcelain crucible and heated for one hour at 105° C. in a constant-temperature oven (Fig. 2). The crucible is then removed from the oven, covered, and cooled in a desiccator over sulphuric acid. The loss in weight multiplied by 100 is counted as the percentage of moisture.

¹Holmes, J. A., The sampling of coal in the mine. 1911. 18 pp.

The oven used is a double-walled copper cylinder, closed at one end and having a double-walled door at the other. The space between the outer and the inner wall is filled with a solution of glycerin in water (specific gravity, 1.19 at 15° C.), the proportions being so adjusted that the boiling solution maintains a tem-

perature of 105° C. in the interior of the oven. There is free circulation space for this glycerin solution on the sides and at one end of the oven. A return condenser keeps the concentration constant. A current of air, dried by passing through sulphuric acid and preheated by passing through a copper tube encircling the oven between the walls, is forced through the inner chamber of the oven over the samples; it takes up moisture from the samples and escapes through a small opening in the door of the oven. The air is forced through the oven at a rate sufficient to change the total volume of air in the oven from 8 to 10 times in one hour. With this oven no trouble is experienced in maintaining a constant temperature of 105° C.

Volatile Matter.—A 1-gram sample of the fine (60-mesh) coal is weighed into a bright, well-burnished, 30-gram platinum crucible with a close-fitting cover. The crucible and contents are heated upon a platinum triangle for seven minutes over a Bunsen flame 20 cm. high. The crucible should be so placed in the triangle that its bottom is 6 to 8 cm. above the top of the burner. To protect the crucible from the effects of drafts, it is put in a sheet-iron chimney (Fig. 3) of special design. After being heated seven minutes the crucible is cooled and weighed. The loss in weight minus the weight of moisture determined at 105° C. times 100 equals the percentage of volatile matter.

It should be clearly understood that the volatile matter thus determined does not represent any definite compound in the coal. The method of determination is wholly conventional, and any variation in temperature or rate of heating will change the amount of volatile matter determined. Even with strict adherence

perature of 105° C. in the interior of the oven. There is free circulation space for this glycerin solution on the sides and at one end of the oven. A return condenser keeps the concentration constant. A current of air, dried by passing through sulphuric acid and preheated by passing through a copper tube encircling the oven between the walls, is forced through the inner chamber of the oven over the samples; it takes up moisture from the samples and escapes through a small opening in the door of the oven. The air is forced through the oven at a rate sufficient to change the total volume of air in the oven from 8 to 10 times in one hour. With this oven no trouble is experienced in maintaining a constant temperature of 105° C.

Ash.—Ash is determined in the residue of dried coal from the moisture determination. The porcelain crucible containing this residue is placed in a muffle furnace and slowly heated until the volatile matter in the coal is driven off. The object of this slow heating is to avoid coking the sample and thus making its burning difficult; furthermore, if a coal that is high in volatile matter is rapidly heated, the gas generated has a tendency to explode within the capsule and thus carry off mechanically portions of the ash. The ignition in the muffle is continued, with occasional stirring of the ash, until all particles of carbon have disappeared. The crucible with its contents is then taken from the muffle, cooled in a desiccator, and weighed, after which it is placed in the muffle, heated for half an hour, cooled in a desiccator, and weighed again. If the

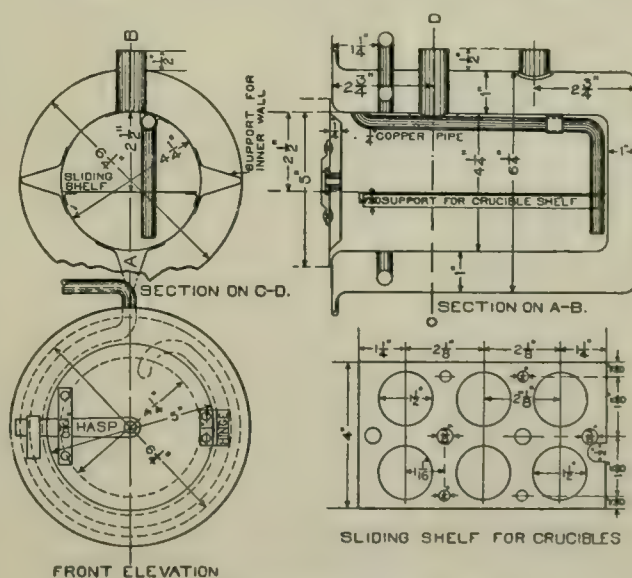


Fig. 1—Details of Drying Oven.

Fig. 2—Details of Moisture Oven.

to the official method, variations as large as 2 per cent are likely to occur in different laboratories where different kinds of gas are used, as is shown by the experiments of Fieldner and Davis.² Natural gas, because of its requiring a larger proportion of air for complete combustion, should be supplied at a pressure of not less than 10 ins. of water to a good natural-gas

²Jour. Ind. and Eng. Chem., vol. 2, July, 1910, p. 301.

burner admitting ample air; otherwise the flame temperature will be too low.

Lignites and coals high in moisture must be heated at a low temperature until all the moisture is driven out in order to avoid mechanical losses from material thrown out of the crucible by the rapid escape of steam and volatile matter.³ This preliminary heating for four to six minutes is followed by the usual seven-minute application of the full 20-cm. flame.

Sulphur.—Sulphur is determined by the Eschka method. "Eschka mixture" is made by thoroughly mixing light calcined magnesium oxide (MgO), two parts, with anhydrous sodium carbonate (Na_2CO_3) one part. A 1-gram sample of 60-mesh coal is thoroughly mixed in a 30-c.c. platinum crucible with about 2 grams of Eschka mixture, and about $\frac{1}{2}$ gram of Eschka mixture is spread over the top to form a cover. The crucible with its contents is placed on a triangle in a slanting position and the mixture is burned out over an alcohol, gasoline, or natural-gas flame. Arti-

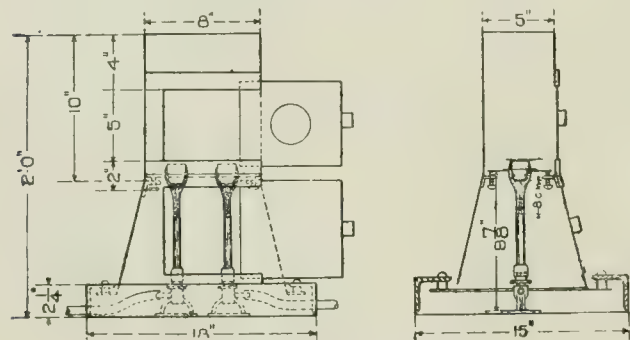


Fig. 3—Stand for Burner.

ficial gas as a rule contains so much sulphur that its use may introduce an error in the determination, owing to the uncertainty regarding the quantity of sulphur taken up by the mixture. In starting the burning a very low flame must be used to avoid driving off volatile matter so fast that the sulphur escapes unburned. Even a small loss of sulphur dioxide (SO_2) may be detected by its pungent odor. The contents of the crucible should never be heated hot enough to cause the blackening of the Eschka-mixture cover.

After the crucible has been heated very slowly and cautiously for about 30 minutes the heat is increased, and after the crucible becomes red hot the contents are stirred occasionally until all black particles are burned out, a condition which indicates that the process is complete. The crucible and contents are then allowed to cool, and the contents are transferred to a 200-c.c. beaker and digested with 75 c.c. of hot water for at least 30 minutes. Filtration into a 300-c.c. beaker follows; the insoluble residue is washed twice with hot water by decantation, and after being transferred to the filter paper is washed with small quantities of hot water until the volume of solution in the 300-c.c. beaker is about 200 c.c. About 4 c.c. of saturated bromine water (or a slight excess) and enough concentrated hydrochloric acid (HCl) to make the solution

slightly acid are added. The solution is next boiled, and the sulphur is precipitated as barium sulphate ($BaSO_4$) by adding, slowly from a pipette with constant stirring, 20 c.c. of a hot 5 per cent solution of barium chloride ($BaCl_2$). The solution containing the precipitate is allowed to stand for at least two hours at a temperature just below boiling. It is then filtered through an ashless filter paper and washed first with hot water containing 1 c.c. of hydrochloric acid (HCl) per liter, and then with pure hot water until a silver nitrate solution shows no precipitate with a drop of the filtrate. Test for excess barium chloride is made by adding a few drops of sulphuric acid solution to the filtrate. The precipitate is then ignited in a weighed porcelain crucible, free access of air being allowed and the paper being folded over the precipitate only loosely to prevent spattering. The paper should be smoked off very gradually at first and the final heating should not be above a dull redness. After the paper is burned off completely the heating is continued for a few minutes, when the crucible is cooled and weighed. The weight of barium sulphate multiplied by 13.74 equals the percentage of sulphur in the sample.

Carbon and Hydrogen.—The determination of carbon and of hydrogen is made from a weighed quantity of sample in a 25-burner combustion furnace of the Glaser type. The products of combustion are thoroughly oxidized by being passed over red-hot copper oxide and lead chromate, and are fixed by absorbing the water in a weighed Marchand tube filled with granular calcium chloride ($CaCl_2$) and by absorbing the carbon dioxide in a Liebig bulb containing a 30 per cent solution of potassium hydroxide (KOH).

The apparatus used consists of a purifying train, in duplicate, a combustion tube in the furnace, and an absorption train. The purifying train consists of the following purifying reagents arranged in order of passage of air and oxygen through them: Sulphuric acid, potassium hydroxide solution, soda lime, and granular calcium chloride. One of the trains is for air and one for oxygen. In the sulphuric-acid and potassium-hydroxide scrubbing bottles the air and the oxygen are made to bubble through about 5 mm. of the purifying reagent. Both purifying trains are connected to the combustion tube by a Y tube, the joint being made tight by a rubber stopper.

The combustion tube is made of hard Jena glass. Its internal diameter is about 15 mm., and its total length is 1 meter. The first 30 cm. of the tube is empty; following this empty space is an asbestos plug (acid washed and ignited) or in its place a roll of copper gauze may be used; the next 40 cm. is filled loosely with copper-oxide wire; a second asbestos plug separates the wire from 10 cm. of fused lead chromate, which is held in place by another asbestos plug 20 cm. from the end of the tube. The end of the tube is drawn out for rubber-tubing connection with the absorption train.

³U. S. Geol. Survey Bull. 323, pp. 6-7.

The absorption train consists, first, of a Marchand tube filled with granular calcium chloride (CaCl_2) to absorb moisture. This tube is followed by a Liebig bulb containing a 30 per cent postassium-hydroxid (KOH) solution, in which any possible impurities, as ferrous iron or nitrates, have been oxidized by a little potassium permanganate (KMnO_4). A guard tube, containing soda lime and granular calcium chloride, is attached to the Liebig bulb to absorb any carbon dioxide escaping the potassium-hydroxide solution and any water evaporating from that solution.

The train is connected to an aspirator which draws the products of combustion through the entire train. A guard tube of calcium chloride prevents moisture from running back into the absorption train. The suction is maintained constant by a Mariotte flask. The advantage of aspirating the gases through the train rather than forcing them through by pressure is that the pressure on the rubber connections is from the outside, so that gas-tight connections are more easily maintained than if the pressure is on the inside of the tube. The connections are made as tight as possible. The usual test for tightness is to start aspiration at the rate of about three bubbles of air per second through the potash bulb, and then to close the inlet for air and oxygen at the opposite end of the train; if there are no more than five bubbles per minute in the Mariotte flask the apparatus is considered tight.

Before starting a determination when the train has been idle some hours, or after any changes in chemicals or connections, a blank is run by aspirating about 1 liter of air through the train, which is heated in the same manner as if a determination on coal were being made. If the Liebig bulb and the tube containing calcium chloride show a change in weight of less than 0.5 mg. the apparatus is in proper condition for use.

A 0.2 gram sample (crushed to 60-mesh) is weighed into a platinum or porcelain boat. The boat and sample are placed in a glass weighing tube closed with a stopper to prevent moisture changes. The absorption tubes are connected and the boat and sample are transferred from the weighing tube to the combustion tube, which should be cool for the first 30 cm. The copper oxide should be red hot and the lead chromate at a dull-red heat. The transfer of the boat from weighing tube to combustion tube should be made as rapidly as possible. As soon as the boat is in place (near the asbestos plug at the beginning of the copper oxide) the stopper connecting with the purifying train is inserted and the aspiration started with pure oxygen gas at the rate of three bubbles per second. One burner is turned on about 10 cm. back from the boat, and the aspiration is continued carefully until practically all the moisture is expelled from the sample. The heat is then increased very gradually until all the volatile matter has been driven off. In driving off the volatile matter the heat must be applied gradually in order to prevent a too rapid evolution of gas and tar, which may either escape complete combustion or may be driven back

into the purifying train. The heat should be slowly increased by turning on more burners under the open part of the tube until the sample is ignited; then the temperature can be increased rapidly, but care should be taken not to melt the combustion tube. The aspiration with oxygen is continued for two minutes after the sample ceases to glow, when the heat is then turned off and about 1,200 c.c. of air is aspirated. The absorption bulbs are then disconnected and weighed. The increase in weight of the calcium chloride tube times 55.55 equals the percentage of hydrogen. The increase in weight of the potassium hydroxide bulbs times 136.36 equals the percentage of carbon. The ash in the boat is weighed and carefully inspected for any unburned carbon which would destroy the value of the determination.

Nitrogen.—The well-known Kjeldahl method is used in determining nitrogen. One gram of the coal sample is boiled with 30 c.c. of concentrated sulphuric acid (H_2SO_4) and 0.6 gram of mercury until all particles of coal are oxidized and the solution nearly colorless. The boiling should be continued at least two hours after the solution has reached the straw-colored stage; then crystals of potassium permanganate (KMnO_4) are added, a few at a time, until a permanent green color remains. After cooling, the solution is diluted to about 200 c.c. with cold water. Twenty-five cubic centimeters of potassium sulphide (K_2S) solution (40 grams K_2S per liter) is added to precipitate the mercury; to prevent bumping 1.0 gram of granular zinc, and, to prevent frothing, a piece of paraffin about the size of a brass 1-gram weight are also added. Enough saturated sodium hydroxide (NaOH) solution (usually 80 to 100 c.c.) to make the solution distinctly alkaline is next added and the flask is at once connected with the condenser. The ammonia (NH_3) is distilled over into a measured amount of standard sulphuric acid solution, to which has been added sufficient cochineal indicator for titration. The solution is distilled until about 200 c.c. of distillate has passed over, and the distillate is titrated with standard ammonia (NH_4OH) solution (20 c.c. NH_4OH solution = 10 c.c. H_2SO_4 solution = 0.05 gram nitrogen).

The transfer to a distillation flask may be avoided by the use of a 500 c.c. Kjeldahl flask for digestion of the coal, connection being made direct from the Kjeldahl digestion flask to the condensing apparatus.

Phosphorus.—For the determination of phosphorus in coal or coke, a sample weighing 6.52 grams is burned to ash in the muffle furnace. The ash is mixed with four to six times its weight of sodium carbonate plus 0.2 gram of sodium nitrate, and is fused at the highest temperature of the blast lamp. The fused mass is dissolved in water, acidified, and evaporated to dryness. The residue is taken up in hydrochloric acid, and the phosphorus determined in the usual way, either by weighing or by titrating the yellow precipitate with permanganate.

DETERMINATION OF THE CALORIFIC VALUE OF COAL.

Determination of the calorific value of coal is made with the bomb calorimeter. The method used is applicable to the Mahler, Atwater, Williams, and Emerson bomb calorimeters, all of which are in use in the laboratories of the bureau. The following is a brief description of the details of operation:

A 1-gram sample of coal (60-mesh) is placed in a platinum tray, the bottom of which is covered with a piece of asbestos paper that has been washed and ignited. The use of this asbestos mat avoids trouble in completely burning anthracite coal. One of the platinum terminals of the firing circuit is attached to the tray. The terminals are connected by a piece of iron wire (platinum wires should be used when the bomb is platinum-lined) 105 mm. long, 0.16 mm. in diameter, and weighing about 13 mg. The ends of the wire are attached to the platinum terminals, which must be clean, simply by wrapping the wire tightly around them. The iron wire is bent down so as to touch the coal sample on the mat within the tray. The tray is then placed in the bomb and the lid screwed down tightly against the lead gasket. Oxygen is forced into the bomb until the manometer recording the pressure within the bomb reads 18 to 20 atmospheres, when the needle-point valve is closed just tight enough to prevent leakage of gas. The oxygen must be admitted very slowly to avoid blowing any particles of coal dust out of the tray. With some extremely light materials, such as peat, it is best to briquet the sample and take a weighed portion of the broken briquets instead of using the powdered sample.

The bomb filled with oxygen is placed in the brass bucket containing 2,000 to 2,500 grams of distilled water, depending upon the type of calorimeter used, the bucket having been previously placed in the insulated jacket. The stirring apparatus is adjusted so that it touches neither bucket nor bomb, and the thermometer is inserted so that the bulb is about 5 cm. from the bottom of the bucket and is in contact with no metal parts of the apparatus. The outside terminals of the bomb are connected with wires leading to the switch. After the stirrer has been in motion for about a minute, or when the water has been thoroughly mixed, the first reading of the thermometer is taken by means of a reading telescope attached to a cathetometer. The thermometer is graduated to $0.01^{\circ}\text{C}.$, and the readings can be interpolated to $0.001^{\circ}\text{C}.$ For the accurate calorimetric work the thermometers should be calibrated to $0.001^{\circ}\text{C}.$ The stirring should be continued at a uniform rate throughout the determination, and should be sufficiently rapid to insure thorough mixing.

The actual determination may be divided into three periods—the preliminary period, the combustion period, and the final period. The preliminary period usually requires five readings taken one minute apart, or until the rate of change per minute is nearly constant. After taking the fifth reading the current at

75 volts is turned on for about one-half second. This is the beginning of the combustion period. The first two readings in this period are taken one-half minute apart because the change in temperature is so great. The temperature rises to a maximum and then begins to fall; after its rate of fall becomes uniform, readings are taken every minute for five or six minutes. The final reading of the combustion period is the first reading after the rate of fall becomes uniform.

The figures in Table I are from an actual determination and show the method of calculating the result, and the corrections applied.

TABLE I.—METHOD OF CALCULATING FROM CALORIMETER READINGS.

(Sample No. 10743. Weight 1.0000 gram.)			
Time.	Readings.		
p. m.	$^{\circ}\text{C}.$		
1.00			
.54	23.874	.0058 rate of change in preliminary period	26.463
.55	23.879		23.897
.56	23.885	Observed temperature change	2.566
.57	23.892	Thermometer correction	.002
.58	23.897 + a .0058	+ b .0027 Radiation loss	2.564
			.0066
			2.5706
.58½	24.160 + a .0049	Water equivalent	3000
		+ b .0014	
.59	25.430 + a .0008	Total heat developed (calories)	7,711.8
		+ b .0006 Correction	41.4
.60	26.280 — a .0020	Heat developed by combustion of sample (calories)	7,670.4
		— b .0023	
2.01	26.439 — a .0025	— b .0026	
.02	26.463 — a .0026	— b .0026	
.03	26.466 — a .0026	— b .0026	
		— .0066 algebraic sum.	
.04	26.463		
.05	26.460		
.06	26.458 —	.0026 rate of change in final period.	
.07	26.455		
.08	26.454		
.09	26.450		
Wire burned = 11.2 mg.			Calories.
Titer (1 c.c. = 5 cal.), 2.5 c.c.			= 19.0
Sulphur (0.01 gm. = 13 cal.), 0.0076 gm.			= 12.5
			= 9.9
Room temperature = $24^{\circ}\text{C}.$			41.4

^aComputed rate per minute of temperature change at each reading.

^bTemperature correction for heat loss during each interval.

The reading 23.874° , taken at 1:54 p. m., is the first reading of the preliminary period. The temperature reading 23.897° is the last reading of the preliminary period and was taken at 1:58 p. m., 4 minutes after the first reading; hence $23.897^{\circ} - 23.874^{\circ} = 0.023^{\circ}$, total change in temperature during the preliminary period; also $0.023^{\circ} \div 4 = 0.0058^{\circ}$, rate of change per minute during the preliminary period.

The rate of change per minute in the final period is found in like manner to be -0.0026° ; hence $+0.0058^{\circ} - (-0.0026^{\circ}) = 0.0084^{\circ}$, change in rate during the combustion period.

The observed change in temperature during the combustion period is 2.564° ; the change in rate per degree of temperature change in the combustion period

$$0.0084^{\circ}$$

is therefore equal to $\frac{\quad}{2.564^{\circ}} = 0.0033^{\circ}$.

$$2.564^{\circ}$$

The change in temperature during the first half minute of the combustion period is 0.273° , and

$$0.273^{\circ} \times 0.0033^{\circ} = .0009^{\circ}, \text{ change in rate during first half minute of combustion period.}$$

$$0.0058^{\circ} - 0.0009^{\circ} = .0049^{\circ}, \text{ rate of temperature change at reading at } 1.58\frac{1}{2} \text{ p. m.}$$

The rate of change for each succeeding reading in the combustion period is calculated in the same way.

The temperature correction for the heat loss during the half-minute readings is made by dividing the algebraic sum of the rates by 4, and for the minute readings the algebraic sum is divided by 2, because the temperature correction for heat loss during each interval is the mean rate per minute of temperature change multiplied by the time of the interval in minutes. For example, at 1.58 p. m. the rate per minute of temperature change is $+0.0058^{\circ}$, and at $1.58\frac{1}{2}$ the rate per minute of temperature change is $+0.0049^{\circ}$; therefore the mean rate per minute of temperature change for the one-half minute interval is

$$\frac{0.0058 + (+0.0049)}{2} = +0.0054^{\circ},$$

and $\frac{1}{2} \times (+0.0054) = +0.0027$, which is the correction for heat loss taking place during the half-minute interval. The algebraic sum of all the temperature corrections for heat loss during each interval is added to the observed temperature change after corrections have been made for the errors in the thermometer; this figure multiplied by the water equivalent of the apparatus gives the total heat developed. Further corrections must be deducted for heat due to formation of aqueous nitric acid and sulphuric acid and to combustion of the iron wire. The correction for iron wire is 1.7 calories per milligram. The correction for sulphur burned to sulphuric acid is 13 calories per 0.01 gram of sulphur. The correction for nitrogen to aqueous nitric acid is made by titrating the acidity of the bomb liquor with standard ammonia solution (0.00574 gram NH_3 per c.c.), and is equivalent to 5 calories per cubic centimeter.

After the combustion of the coal in the calorimeter the bomb is washed out thoroughly and the washings are titrated with standard ammonia solution (0.00574 gram per c.c.), methyl orange being used as an indicator. The acidity is due to the nitric acid (HNO_3) formed from the nitrogen of the coal and the nitrogen of the air in the bomb, and also to the sulphuric acid formed from the combustion of the sulphur in the coal. The sulphur can be easily determined by precipitation as barium sulphate. It is convenient to make the ammonia solution of such strength that 1 cubic centimeter is equivalent to 0.00473 gram of ni-

trogen, for this weight of nitrogen burned to nitrogen pentoxide (N_2O_5) plus water generates 5 calories of heat. The figures are derived as follows:

The calorific value of nitrogen burning to N_2O_5 + water is 1,058 calories per gram.

$$1,058 \text{ calories} : 5 \text{ calories} :: 1 \text{ gram} : 0.00473 \text{ gram.}$$

Therefore 0.00473 gram of nitrogen generates 5 calories of heat when burned to aqueous nitric acid.

The ammonia solution is made up according to the equation.

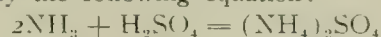


$$\text{Since } \text{N} = 14, \text{ and } \text{NH}_3 = 17,$$

$$14 : 17 = 0.00473 \text{ gram} : 0.00574 \text{ gram.}$$

Therefore 0.00574 gram of NH_3 is equivalent to 0.00473 gram of nitrogen, which when burned to aqueous HNO_3 generates 5 calories of heat. The standard solution contains 5.74 grams of NH_3 per liter. The solution, when used to titrate the bomb liquor after combustion of a coal sample, must satisfy not only the nitric acid formed, but also any sulphuric acid resulting from the combustion of the sulphur in the coal.

The strength of the ammonia solution in terms of sulphur in the form of sulphuric acid (H_2SO_4) is determined by the following equation:



$$2\text{NH}_3 : \text{S} = 34 : 32 = 0.00574 \text{ gram } \text{NH}_3 : 0.0054 \text{ gram S.}$$

The heat of combustion of sulphur to aqueous H_2SO_4 is 4,450 calories per gram of sulphur. This reaction takes place in the bomb calorimeter, when the fuel is burned in an atmosphere of oxygen under high pressure.

In the ordinary combustion of coal under a boiler, the sulphur burns to sulphur dioxide (SO_2), the heat of formation of which is 2,250 calories per gram of sulphur. The difference between these two calorific values (4,450 calories — 2,250 calories) is 2,200 calories per gram of sulphur. Therefore it is necessary to make a correction of 2,200 calories per gram of sulphur in the calorimeter determinations, owing to the formation of aqueous sulphuric acid. Since 1 c.c. of the ammonia solution is equivalent to 0.0054 gram of sulphur, 0.0054 times 2,200 equals 11.9 calories, the heat correction to be made if all the acidity of the liquor from the bomb represented H_2SO_4 .

Hence the ammonia solution containing 0.00574 gram NH_3 per c.c. is equivalent to 5 calories for nitrogen converted to aqueous HNO_3 or to 11.9 calories for sulphur converted to aqueous H_2SO_4 . A further correction, therefore, must be applied for the sulphur that is determined separately. This correction is a function of the difference between the value of the ammonia solution in terms of sulphur (11.9 calories), and its value in terms of nitrogen (5 calories) or 6.9 calories. The difference, 6.9, divided by 0.0054, the value of 1 c.c. of ammonia solution in grams of sulphur, equals 1,276 calories per gram of sulphur, or 13 calories for each 0.01 gram of sulphur.

The total acidity correction is, then, the cubic centimeters of NH_3 solution multiplied by 5 (the factor for nitric acid) plus the centigrams of sulphur multiplied by 13.

Standardization of the Calorimeter.—The first factor to be considered in calorimetric work is the cor-

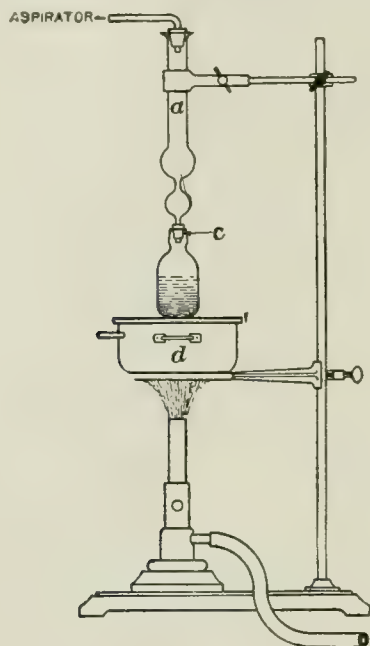


Fig. 4—Arrangement of Pycnometer.

rect determination of the water-equivalent value of the apparatus. This equivalent may be determined by a number of methods, as follows:

1. By adding the products of the weight of the different parts of the apparatus times their specific heat.

2. By generating heat within the bomb by passing a measured electric current through a known resistance for a given length of time.

3. By adding definite weights of water at different temperatures to the system and noting the corresponding temperature changes.

4. By varying the quantity of water surrounding the bomb, thus keeping the heat generated within the bomb constant.

5. By the combustion of a substance of known calorific value. This is a very convenient and accurate method of standardization. Samples of pure cane sugar, benzoic acid, and naphthalene may be obtained from the Bureau of Standards.

DETERMINATION OF THE TRUE SPECIFIC GRAVITY OF COAL AND COKE SUBSTANCE.

To determine the true specific gravity of coal and coke substance, the procedure is as follows: A sample of the 60-mesh coal, weighing approximately 3.5 grams, is dried at 105°C ., and introduced into a 50-c.c. pycnometer with about 30 c.c. of distilled water. In order to avoid loss of particles of the sample during boiling, a one-bulb 6-in. drying tube (a, Fig. 4) is connected with the pycnometer by means of a small

piece of pure gum tubing (c). The other end of the drying tube is connected with the aspirator. Suction is applied and the contents of the flask are gently boiled on the water bath (d) under partial vacuum for three hours in order to expel all air from the sample. The pycnometer is then detached, almost filled with boiled and cooled water, allowed to cool to the temperature of the balance room, stoppered, and weighed. The temperature of the contents of the pycnometer are taken immediately after weighing. Each pycnometer is accurately calibrated and a table is constructed giving its capacity in grams of water at different temperatures.

The true specific gravity is determined by use of the following formula:

$$\text{True specific gravity} = \frac{W}{W - (W' - P)}$$

in which

W = weight of coke

W' = weight of pycnometer + coke + water to fill

P = weight of pycnometer + water to fill.

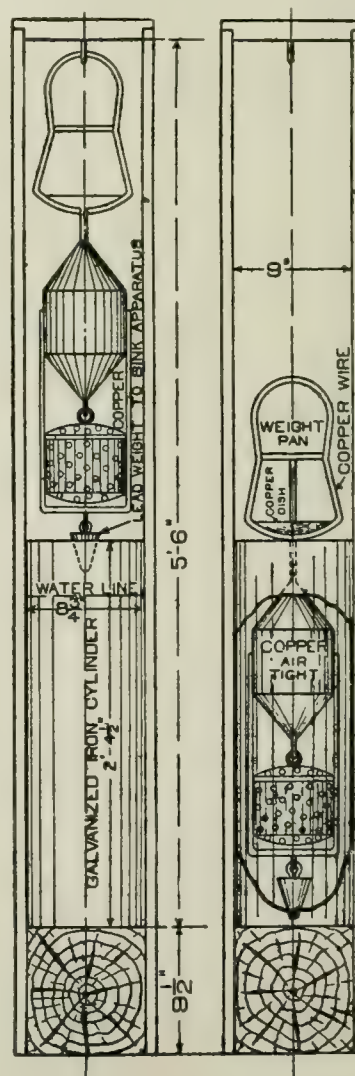


Fig. 5—Apparatus for Determining Apparent Specific Gravity.

DETERMINATION OF THE APPARENT SPECIFIC GRAVITY.

The apparatus used for determination of the apparent specific gravity consists of a galvanized iron cylinder (Fig. 5), which is filled with water to the water line, as indicated in the figure. In the cylinder is immersed a hydrometer made of brass. On the top of the hydrometer are two pans. The upper one is used for weights and the lower for the sample. Below the air buoy is a brass cage perforated with many holes to allow the air to escape when the instrument is immersed. The cage carries the sample when it is weighed under water.

The method of determining the apparent specific gravity is as follows: Brass weights are placed on the upper pan until the hydrometer sinks to a mark on the stem between the copper pan and the buoy. The total weight required is recorded. The weights are removed, and about 500 grams of the sample in lump form (about $1\frac{1}{2}$ to 2 in. cubes) is placed in the copper dish. Brass weights are then added until the hydrometer sinks to the mark on the stem. The difference in the weights used gives the weight of the sample in air. The sample is then carefully transferred to the brass cage below the buoy. The weights on the upper pan are now adjusted until the instrument again sinks to the mark on the stem. The weight required to sink the hydrometer to the mark with no sample on the upper pan nor in the brass cage minus the weight required to sink it to the mark with the sample immersed in the cage equals the weight of the coke in water. Then,

$$\begin{aligned} \text{If the weight of the sample in air} &= x \\ \text{and the weight of the sample in water} &= y, \\ &x \\ \text{the apparent specific gravity} &= \frac{x}{x-y} \end{aligned}$$

And

$$100 \times \frac{\text{apparent specific gravity}}{\text{true specific gravity}} = \text{percentage by volume of coke substance.}$$

Also,

$$100 - \text{percentage by volume of coke substance} = \text{percentage by volume of cell space.}$$

In making apparent specific gravity determinations of coke the sample should preferably be in lumps of nearly the same size and shape. When the sample is immersed, the hydrometer should be moved rapidly up and down in the water a number of times in order to remove air bubbles. Since coke samples are porous, they take up water rapidly and should not be allowed to remain in contact with water more than five minutes during a determination. By observing the above-mentioned precautions satisfactory results can be obtained. All samples should be thoroughly dry before specific gravity determinations are made.

A U. S. Consular agent at Freemantle, Western Australia, reports the invention of a new system for generating gas. This is known as the "Autogene" air-gas system. It was invented by P. C. Booty, of Perth, Western Australia, and is a device for manufacturing gas from gasoline and air. The apparatus is simple, consisting mainly of a patent valve and carburetor by means of which gas of uniform quality is automatically supplied to the service irrespective of the fluctuation of the load. No more gas is generated than is needed for immediate consumption. Connected to the valve is an air pump of simple form surmounted by a gasoline tank and air holder. The pump may be operated by a weight-driven, electric, or water motor, or by a hot-air motor supplied with gas from the system. The gas produced is not poisonous, and as there is no storage of gas the insurance companies do not charge extra premiums. The mixture is used for lighting, heating, and power purposes. The light is said to be white and of a very good quality, and there is a total absence of smoke or smell. As the system supplies its own air there is no depletion of oxygen in the room where the gas is being consumed. The outfit is capable of producing 1,200 cubic feet of gas for each gallon of gasoline used.

The U. S. Civil Service Commission, Washington, D. C., will hold an examination on May 8-9 at various cities throughout the country to secure eligibles from which to make certification to fill vacancies as they may occur in the position of junior chemist (explosives) in the Bureau of Mines, Pittsburgh, Pa., at salaries ranging from \$1,200 to \$1,500 per annum, unless it is found to be in the interest of the service to fill such vacancies by reinstatement, transfer, or promotion. Men only will be admitted to this examination. The examination will consist of the subjects mentioned below: (1) Translation from French or German technical works; (2) General chemistry and physics, including calculations; (3) Essay on some subject relating to chemistry of explosives (English composition will be rated on this subject); (4) Chemistry of explosives; (5) Training, experience and fitness. Applicants must show that they have had educational training and experience equivalent to a four years' course in a technical college of good standing, the larger portion of which course is devoted to a study of chemistry, including a considerable amount of laboratory practice, especially in quantitative analysis. Special credit will be given for experience in the analysis or manufacture of explosives.

The coal output of Belgium in 1911 was 23,125,140 tons; the decrease of 802,000 tons from 1910 was due to the new $9\frac{1}{2}$ -hour miner's day. The work day was further reduced to 9 hours from January 1, 1912.

of the pyrometer thermo-couple. In nearly all cases four determinations at temperatures ranging from 200° to 900° were made for each of the materials tested.

From the data obtained as described above, curves

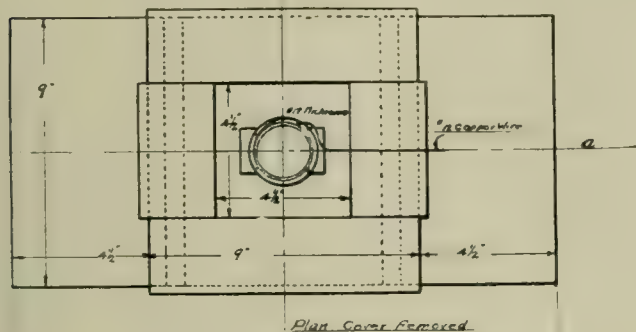


Fig. 2.

were plotted in which the abscissas are temperatures and the ordinates watts.

In Fig. 3 are shown the curves obtained with several different bricks.

No. 2 is a fire brick of moderately good quality, that is to say, it is not of any special make. It was the brick used in constructing the furnace referred to in the paper mentioned above.² The maximum temperature reached in the brick testing furnace was 800°.

No. 4 is the curve for a silica brick. It is interesting

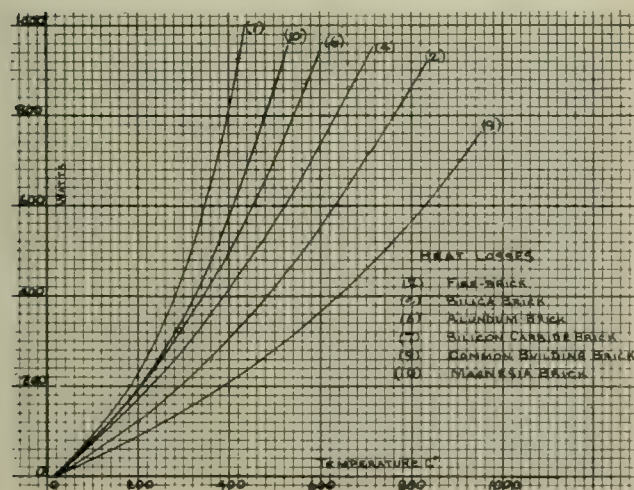


Fig. 3.

to note that in the paper² already referred to it was said:

"It was recognized that silica brick are better heat insulators than fire brick, as may be seen from Wologdine's determinations³ which show that the heat conductivity of silica is 0.0020 and of fire brick 0.0042."⁴

It appears, however, that in spite of its low heat conductivity this particular silica brick is not a satisfactory insulator. The maximum temperature reached with

the silica brick was 670°. The heat loss here was 36 per cent greater than with the fire brick. It is not very safe to theorize as to the cause of this phenomenon, but it looks as though the radiation from the surface of the silica brick is very much greater than from the ordinary fire brick. The vast differences due to the nature of the radiating surface is not so surprising if a familiar household phenomenon is considered, viz., the great difference in the rate of cooling of the common black iron kettle and the polished silver tea pot.

No. 6 was obtained from an alundum brick, one of the highly refractory ones made by the Norton Company. The transmission of heat was so rapid with this brick that the maximum temperature obtained in the furnace was only 570°. This illustrates well the value of such alundum refractories as crucibles, muffles, etc., where it is desirable to have as efficient transmission of heat as possible.

No. 7 is the curve for a brick made of silicon car-

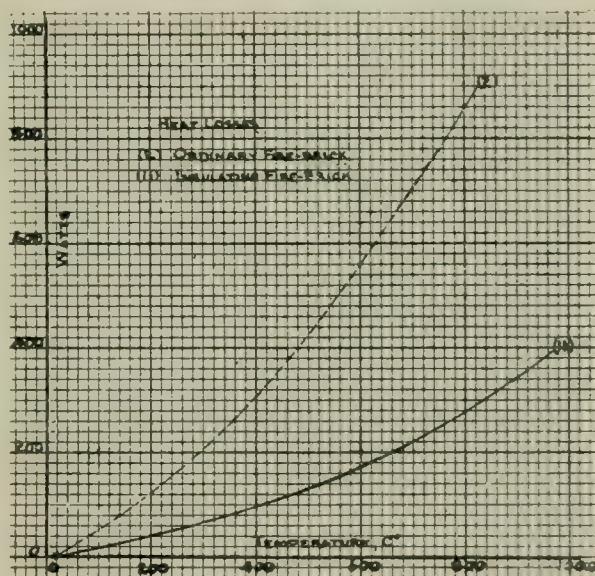


Fig. 4.

bide. The brick is pure silicon carbide, that is, no bond is used in making it. The transmission of heat is extremely good with this brick so that the maximum temperature reached in the furnace was only 420°. Comparing this brick with the fire brick (2) when the temperature in the furnace was the same (420°) it is seen that the rate of escape of energy is 920 watts and 300 watts respectively, or more than three times as great in the case of the silicon carbide brick.

Curve No. 9 is that for an ordinary red building brick of the cheapest kind. It is seen to be the best insulator of any of this lot, the heat losses being as much as 34 per cent less than those for the fire brick (2) at a furnace temperature of 800°.

Curve No. 10 shows the results obtained with a magnesia brick. This was of a standard kind made of brown magnesia and not the Grecian magnesia variety.

²Ibid.

³Electrochemical and Metallurgical Industry, Vol. VI (1909), page 383.

⁴Transactions American Electrochemical Society, Vol. 20, 89 (1911).

In Fig. 4 are shown the results obtained, first with the ordinary fire brick (2) and then after covering the whole furnace built of this brick with a 25 mm. (1 inch) thickness of a special heat insulating material kindly supplied by a well known manufacturer. It will be observed that this material reduced the heat losses by more than 50 per cent.

In Fig. 5 is a comparison of the heat losses obtained with the ordinary fire brick (2) and a brick specially constructed for heat insulation. Here it will be observed that in the case of the special insulating brick the heat losses are reduced 68 per cent.

The first object of this work is to make a study in the quickest way possible of the heat insulating properties of various kinds of brick used in building furnaces, and get some notion of the amount of heat lost with such materials. The ultimate object in view is the production of a heat insulating article, the cost of

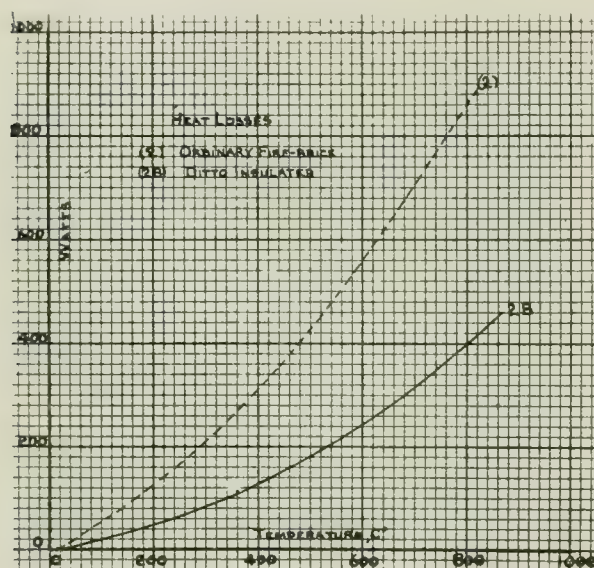


Fig. 5.

which will be less than that of the watt-hours uselessly dissipated through furnace walls.

The foregoing paper represents some of the results obtained in the preliminary investigation of the subject. There have been many data obtained on other bricks made with the object of efficient insulation, and it is hoped that these will be ready for presentation at the autumn meeting of this society.

The present output of the chemical industry in Russia represents the considerable value of \$77,250,000 per year. The principal items of this production are inorganic acids and salts, gunpowder, paints and lacquers, organic dyes, and superphosphates. The chemical factories are nearly always close to the leading industrial centers and consequently frequently far away from the regions producing the raw materials. This circumstance has often led to the importation of raw material from abroad, which, brought by sea, came far cheaper.

ARTIFICIAL SILK.

The production and use of artificial silk is a subject which is hardly appreciated as yet by those not in contact with the industry. In the first processes, the raw material used were so expensive, the process so costly and the product of such poor quality that it seemed to be of small importance. Today it is far from unimportant, and seems destined to replace cocoon silk for all minor purposes. Practically all of the "silk" braids and trimmings, knit neckties, and embroidery silks are made of "vegetable fiber." The gloss and sheen of this artificial product surpass most silk and an amateur cannot tell the false from the real article. True synthetic silk has been made, it is claimed, but is too expensive for any commercial purposes. But the imitation, which has no relation to the original in chemical composition to the original, can be manufactured quite cheaply from our most common fiber supply, namely, wood pulp.

The first process used commercially was devised by Chardounet of Paris, France. He struggled for many years to put his process on the market, at last succeeded, and now, it is said, has become very wealthy from it. His first process utilized the lower nitrates of cellulose formed by the action of nitric and sulphuric acids on cellulose under carefully regulated conditions. This product called pyroxylin was freed from acids and carefully dried, after which it was dissolved in a mixture of alcohol and ether to form a sirupy solution. This solution, forced through very fine orifices into water, formed a jelly-like thread which was wound on a large drum and dried. In drying it shrank considerably and the stretching so produced gave the fiber its high lustre. This first product was explosive, however, and was too dangerous for extensive use. A process for denitrating the thread was soon discovered and now many are in use. The foremost of them today is to pass the thread through a solution of ammonium sulphide, which effectually denitrates it and leaves a thread of almost pure cellulose without depriving it of any of its lustre. In the ordinary process several of these threads are twisted together to form the yarn of commerce.

Further improvements in this process have been made by Dr. Lehner of Zurich and enormous plants at Besancon, France; Frankfort, Germany; Zurich and places in Switzerland and Austria are turning out thousands of pounds of Chardounet silk daily. The raw materials for this process must be quite pure on account of the combustible tendency of the intermediate product pyroxylin, but it still enters into strong competition with the newer methods which use cheaper raw materials.

The second process to be developed commercially was based on the fact that a solution of cuprammonium (a copper salt with ammonia) dissolves cellulose readily. The cellulose is readily reprecipitated from

these solutions by alcohol or brine and many other compounds. The apparatus used is similar to that of the Chardounet process except that the thread is coagulated in brine instead of water or air. The copper is washed out from the threads and they are wound together and dried as in the previous method. This product is slightly superior in most ways to the Chardounet silk and many plants are using it exclusively.

The third process, which is now generally conceded to be the best, is the "viscose" process of Cross and Bevan (English). Almost any material may be used from the commonest wood pulp to the best cotton rags. They are first treated with caustic soda as in the process of mercerizing cotton. The excess alkali is drained off and carbon disulphide is added in a closed vessel. The amount of carbon disulphide required is about 40 per cent of the weight of pulp. This dissolves the fiber to form a gummy mass which is completely soluble in weak alkali. This may be considered as a solution of cellulose xanthate and is generally filtered from mechanical impurities by passing through cotton wadding and cheese cloth.

The machine for spinning is somewhat different from the earlier ones. The clarified solution passes to a small platinum cap dipping into an acid bath. In the bottom of the cap there are 15 to 18 holes of about .004 inches diameter. The solution passes through these into the acid, which neutralizes the alkali and coagulates the threads which pass over a bobbin into a small hole in the top of a box revolving at about 1,500 R.P.M. The centrifugal force throws the filaments away from the center and winds them up, putting a slight twist into the resulting yarn. The yarn is wound into bundles or skeins from the "cake" on the inside of the centrifugal. This method has the advantage of handling the threads less before they are dried and produces a stronger yarn.

All of the artificial silks absorb dyestuffs readily and many shades accentuate the high lustre. Great care must be taken in the dyeing as the filaments are very weak when wet and could be easily ruined. As soon as it dries again, it regains its original strength and lustre. Table I, prepared by Haller, a French expert, gives the figures for the various artificial silks, cotton and silk:

TABLE I.

	Absolute strength in kilograms per millimeter of diameter.	
	Dry thread.	Wet thread.
Cotton, ordinary thread.....	11.5	18.6
Cocoon or real silk, raw (in the gum)....	50.4	40.9
Cocoon or real silk, boiled off (gum recovered)	25.5	13.6
Cocoon or real silk, dyed black and weighted to 111 per cent.....	12.0	8.0
Artificial silk, French nitro-cellulose—Chardounet	14.7	1.7
Artificial silk, German nitro-cellulose—Lehner	17.1	4.3
Artificial silk, French Cupra-ammonium—Pauly	19.1	3.2
Artificial silk, English viscose—Stearns....	21.5	3.5

When dry the threads of artificial silk are very small as one pound of some sizes contain 600 miles of individual filament to the pound. Most of the yarn contains about 33,000 yards to the pound with 15 or 18 filaments twisted together. It has been calculated that the daily output of the world's factories is over 3,000,000 miles of filament per day, and forms about 20 per cent of the world's consumption of silk.

There are several new plants starting in the United States, one of the largest being at Chester, Pa. The companies are spending enormous sums of money both in Europe and America for perfecting the processes, both of solution and spinning. All the forms of soluble cellulose are progressive solutions and great care must be taken to spin the mixture at exactly the right moment to get the best results. In consequence it is necessary to keep all the rooms for mixing and aging the solutions at a constant temperature. There are many similar details to be developed and put into practice, but it is evident that the industry is well established and will soon be as thoroughly standardized as other chemical industries are today.

Figures compiled by the U. S. Bureau of Manufactures show that the total output of fusel oil in the United States was 110,792 gals. during 1910, the last year for which figures have been compiled by the United States Internal Revenue officials. This figure was exceeded only by the record year, 1907, when 124,709 gals. were produced. As the production of spirits distilled from other materials than fruit increased from 163,893,960 gals. in the fiscal year ended June 30, 1910, to 175,402,396 gals. in the fiscal year 1911, it is probable that the 1911 output of fusel oil also showed a gain. Illinois ranks first in the production of proof spirits and fusel oil, Ohio second, and Louisiana third. In the first two states, alcohol is produced chiefly from grain, while in Louisiana molasses is the sole source. The imports of fusel oil into the United States amounted to 4,953,952 lbs., valued at \$598,199 during the fiscal year 1910, and 5,231,252 lbs., valued at \$842,916, in 1911. European Russia ranked first as a source of supply, with Germany second, these countries supplying, respectively, 1,342,282 and 1,573,902 lbs. in 1911. It is estimated that the maximum amount of fusel oil obtained in the distillation of proof spirits is about two-tenths of 1 per cent. During the fiscal year 1911, the production of spirits from molasses amounted to 21,634,257 gals., produced from 41,014,190 gals. of molasses. There were 17 molasses distilleries in operation during that period, 6 in Massachusetts, 3 each in California and Louisiana, and 1 each in Hawaii, Kentucky, Michigan, New York, and South Carolina. Louisiana led in the production of spirits from molasses, followed by Michigan, New York, and South Carolina, in the order named.

NATURAL AND ARTIFICIAL INDIGO.

The production of and trade in natural indigo have not yet been as completely destroyed as that of madder, the ground root of the madder plant, formerly cultivated in the south of France, Holland and the countries bordering on the Mediterranean and so largely used formerly by calico printers, dyers, carpet manufacturers and others. But its production has been seriously curtailed and it would appear to be only a question of time for its production to become unprofitable. The decreased demand is entirely due to the competition of synthetic indigo, a chemical product, which was invented by Professor Bayer, the well-known German chemist, some fifteen years or so ago. It was first offered to consumers in 1897, and has practically superseded natural indigo in America and Europe. During the last fifteen years the process of manufacture has been greatly improved and the synthetic dye, which is generally known as indigotin, is now firmly established in most of the markets of the world. Natural indigo is mainly produced in India, and about 50 per cent of the now greatly reduced export trade goes to the Middle East, that is to Persia, Egypt and Asiatic Turkey. The demand for natural indigo in Europe and America has dwindled to such limited quantities that it is evident that it is only bought to provide for the necessities of special trades. For general purposes it has obviously been discontinued as a dye, users throughout the dying industry having substituted the artificial product. It is probable that natural indigo only holds its own in Eastern countries on account of the objection to change of the inhabitants and to the innate conservatism of the Eastern mind, as it is doubtful whether it is in any way specially suited to the requirements of those countries. Thus two years ago there was a considerable increase in the export of Indian indigo to Persia, due to the partial prohibition of the synthetic substitute there. It was, however, only a temporary increase, as the export of 2,730 cwt. during 1910 declined to 1,500 cwt. last year. The government's prohibition against the artificial substitute has been withdrawn and indigo dyes of German make are now being introduced, it is cheaper and it is said to be easier to work by many users. Thus India's loss is Germany's gain. The Japanese demand has now also shrunk to vanishing point, as less than 70 cwt. were exported to that country last year.

As in all other commodities price is the ruling consideration. If natural indigo is to hold its own against its artificial competitor, it will have to be offered at a reduced figure. Many experts assert that it is unquestionably superior for the dyeing of woolen and cotton tissues, its superiority is, however, not so great as to render it indispensable and it cannot therefore displace the artificial dye until it can be offered at the same price; at the present time there is a very considerable difference. There may still be a small market for it in America and Europe, but in bulk the general de-

mand has disappeared and in the Middle East it will have to face a real struggle against determined German competition.

The cultivation of natural indigo, both for native use and for export, is practically an Indian monopoly; it was until recent years a most important and prosperous industry, and large areas of land were under cultivation. There were very numerous indigo factories, considerable capital was invested; European managers and expert assistants were engaged and large numbers of natives employed. During the year 1895-96, when the output reached its high water level, the exports exceeded 187,000 cwts., the value of which was \$17,110,000. During the last fifteen years the decline in the value of indigo exports has been continuous and unfortunately the price has fallen to about 50 per cent of that during 1896. During the last decade the decline has been no less than 83 per cent in quantity and about the same in value, possibly rather more. The only encouraging feature about last year's return is a slight rise in the price of indigo from \$97.20 per cwt., the average price during the last six or seven years, to \$99.60 last year.

During 1911 the exports were as follows: To Egypt, 3,230 cwts.; Asiatic Turkey, 2,670 cwts.; Persia, 1,500 cwts.; United States, 1,310 cwts.; Great Britain, 2,980 cwts.; Europe, 4,900 cwts; smaller markets, 330 cwts. The total being 16,920 cwts., a drop of no less than 170,417 cwts. since 1896. No greater disaster except total extinction could occur to a once flourishing industry. The value dropped from \$17,119,000 to \$1,073,000, a total difference of \$16,046,000. Both the quantity and value of last year's exports were the lowest on record and are some 5 per cent less than those of 1910. From 1910 as far back as 1850 the exports every year with only a few exceptions, exceeded \$9,600,000; the loss of interest on capital invested and loss of wages for labor can therefore be computed from the details above. The land in India until recently devoted to indigo production has been reduced in area and may have to be still further curtailed. The manufacture of the dye will have to be limited to the present export and home requirements; the latter amount to about 20,000 cwts. per annum.

In order to recover the lost ground and compete successfully with the German chemical companies they would have to offer their output at the same price; it is doubtful whether that is possible, as the prices now asked scarcely pay for the cost of production. Only a limited number of those formerly engaged in the industry still keep to it. Of the indigo now produced about 75 per cent is grown in Bengal and Behar under the supervision of English planters, who are making heroic efforts to introduce an improved system of cultivation and more economic modes of manufacture. Should these attempts succeed the industry could yet pull through and compete with the artificial product. The Java variety of the plant has been introduced, which produces a larger quantity of leaf and color than

the variety hitherto cultivated. By improved methods a greater percentage of dye may be extracted. The government is also giving a helping hand, a grant in aid is being made for five years of over \$9,600, from 1909 to 1914. The requirements of the markets are also being studied and the opinion has been expressed by competent authorities that if the percentage of dye extracted can be increased and the price thus kept down, the superiority of the natural dye over the artificial may yet induce consumers to give it the preference. It has been asserted that the synthetic indigo is not as permanent as the natural. The next few years will decide the fate of this once prosperous industry, and if the efforts to economize in the cost of production succeed, it may still recover at least a portion of its former prosperity.

THE LOHMANIZING PROCESS FOR COATING IRON AND STEEL.

A new process for providing a protective coating for metals has been introduced lately. This is known as the Lohmanizing process, named after its inventor, Herman J. Lohman. The operations in this process are as follows:

First—Pickle in bath of sulphuric acid to remove rust and scale.

Second—"The Lohman treatment." Dip the material to be treated in Lohman bath containing an amalgamating salt.

Third—Drying.

Fourth—Dip in molten protective alloy which has a temperature of from 950° to 1000° F.

The second operation in the Lohmanizing process is a special treatment to prepare the surface of pores and cavities existing on the surface of metals for adhesion and permeation of the protective metal.

The pickling by sulphuric acid bath, removes rust and scale, prepares the metal for the Lohman bath, which being composed of acid and an amalgamating salt, further cleans the pores and cavities and deposits the scale upon all metallic surfaces, particularly the pores and cavities. Upon removal from the Lohman bath, the treated material is dried and then immersed in molten protective alloy when an amalgam is formed by combination of the amalgamated salt and protective alloy. The treated metal is gradually raised in temperature by the molten alloy which has a temperature of 950 to 1000° F. and when the treated metal reaches temperature of 500° F., the amalgam is broken and the amalgamating almost volatilizes, is released and comes to and passes from the surface of the molten alloy. In its passage from the surface of the treated metal to the atmosphere, the following important results are obtained: The complete surface of the treated metal, including pores and cavities, are left free from all oxidizing agents, as the amalgamating salt joins the protective alloy forming an amalgam. The salt volatilized leaves spaces into which the protective alloy flows, and inasmuch as the complete surface is

clean the alloy adheres thereto. Further, the oxygen present in the pores and cavities and on the surface having a greater affinity for the amalgamating element than for the metal or alloy passes to the atmosphere, thus taking from the bath the minimum natural oxidizing agent, which is the cause of failure in protective methods, as the oxygen in usual processes remains between the treated metal and the protective metal. Oxidation takes place and the protective coating is forced away, the elimination of which is the object sought for and obtained in the Lohman process. An extremely important feature in the Lohman process is the use of an alloy composed of zinc, lead and tin varied in proportion to suit the requirements of service, this being made possible by the presence of the amalgamating element which during its passage to the atmosphere holds the lead on the molten protective alloy in suspension by agitation and without which lead cannot be utilized.

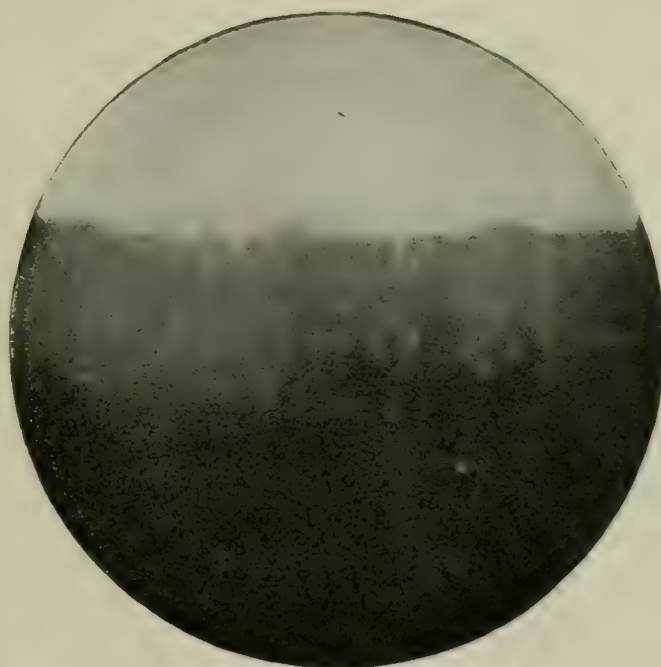


Fig. 1—Micro-photograph of a Lohmanized Sheet.

By the Lohmanizing process, the protective alloy is made to become an actual part of the treated metal. This is shown by Fig. 1. This illustration shows a gradual shading from the original alloy to the base metal, indicating a deep permeation of the treated material by the protective alloy. Long, slender tentacles of alloy have penetrated far into the base metal, filling up perfectly cavities of even the most minute character. If the thin outer coat of alloy on Lohmanized material is ruptured, there still exists over the sheet a protective agency—the deep-seated alloy formed in the permeation of the treated metal by the protective metal, and this alloy cannot be fractured in ordinary uses without breaking the sheet itself.

The Brier Hill Steel Co., Youngstown, O., licensee of the Lohmanizing process, has perfected this method of amalgamating a protective alloy into iron and steel sheets.

THE REGENERATION OF SULPHATED STORAGE CELLS.*

By C. W. BENNETT and D. S. COLE.

In a recent article by Mr. G. A. Perley,¹ a method for curing sulphated storage cells was outlined. The work consisted essentially in experiments on the reduction of lead sulphate by three methods, namely, chemical reduction, electrolytic deposition and reduction, and chemical solution followed by reduction.

By the first method ferrous sulphate and sodium hydroxide, zinc and hydrochloric acid, zinc precipitated electrolytically on the plates, and aluminum with potassium hydroxide, were used as reducing agents. The third reducing agent gave a partial reduction of the sulphate, but it was found that in order to get enough zinc on the plate the current density had to be increased. However, with the increased current density the zinc precipitated on the best conducting portions of the grid and the lead sulphate, which of course formed the non-conducting part, was found to scale off, due to the increased potential difference required to force the higher current through the solution. Straight reduction, therefore, of the lead sulphate was given up.

Since the normal working of a cell lead is left in intimate contact with lead sulphate, which is readily reduced on account of a local couple, probably, it seemed best to try precipitating lead on the lead sulphate and then charge the grid in sulphuric acid. This would give, apparently, normal working conditions. In order to do this, lead was precipitated from lead plumbite, lead fluosilicate, lead acetate, and lead perchlorate solution. The difficulty found here was, that by "treering" the lead flaked off and caused a large amount of shedding and hence loss of the active mass. For this reason this method was considered unsatisfactory.

It was found, rather by accident than otherwise, that a sulphated grid when placed in sodium hydroxide solution became reduced to lead very quickly. In order, therefore, to obtain a sodium hydroxide solution in the pores of the lead plate, where the largest tendency to sulphate is found, electrolysis with sodium sulphate as electrolyte suggested itself at once. The current should be sent through the cell in the direction of charging; sodium hydroxide will be formed at the lead plate, and sulphuric acid at the lead dioxide plate. Thus an alkaline solution will be formed at the cathode and an acid one at the anode.

Now, if the electrode potential for the liberation of hydrogen be measured, a higher voltage is found necessary when an alkaline solution is used than that required for a neutral or acid solution. In the same way a higher voltage is required for the liberation of oxygen in acid solutions. The discharge potentials

for hydrogen and oxygen, respectively, will therefore be increased over those in a straight acid solution. In this way the range of reduction and oxidation will be increased, for a higher voltage can be impressed without the liberation of hydrogen and oxygen. Thus there is a greater tendency to reduce lead sulphate to lead at the lead plate or cathode, and oxidize lead sulphate to lead dioxide at the lead dioxide plate or anode.

When this was tried on cells that were uniformly coated with lead sulphate the results were astonishing. Cells with a capacity of one ampere minute were brought back to their original rated capacity, and in some cases to a capacity over 100 per cent above the original rating.

The concentration of sodium sulphate recommended, which can be varied within wide limits, is 200 grams of the crystallized salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) per liter. The sodium sulphate should fulfill, as regards purity, the requirement for battery acid, that is, it should be chemically pure. It is not necessary to wash out all of the sodium sulphate; the plates need only be dipped once in water. The time of charging in the sodium sulphate solution, for the worst cells, was about 60 hours, at the 8-hour rate.

In order to verify these results on a larger scale than had previously been tried, it was thought desirable to treat a battery belonging to the Department of Electrical Engineering, of Sibley College, Cornell University. The battery consisted of 52 cells, and had been in use for five or more years with very little attention. The cells were used daily by students in the laboratory, throughout the school year, and had been put out of commission for the summer months in the usual way, by removing the plates from the acid, allowing them to stand for 24 hours in water, and then drying. In the spring of 1911 the cells were not allowed to stand long enough in water and hence were very badly sulphated in the fall. They were put back into commission in the usual way, and were found to have very much less than their rated capacity of 60 ampere hours.

During the Christmas holidays just passed the cells were treated by the method above outlined. A capacity and efficiency run was made on the battery before treatment. The power was measured by a watt-hour meter. The current was kept constant at the 8-hour rate, namely, $7\frac{1}{2}$ amperes. The results of this first run are given in Table I below:

TABLE I.—EFFICIENCY AND CAPACITY TEST BEFORE TREATMENT.

Total input, watt hours.....	7,150
Total output, watt hours.....	3,040
Ampere hour output.....	30.6
Energy efficiency, per cent.....	42.5
Energy capacity, of rated,* per cent.....	48.7
Ampere hour capacity, of rated, per cent.....	51.0

From this it can be seen that the active mass of the cells was about half converted into sulphate in the non-available form when used in the ordinary battery acid.

After this the acid was removed, the plates dipped in water, and the jars filled with a solution of chem-

*Paper presented at the 21st General Meeting of the American Electrochemical Society, at Boston, Mass., April 18-20, 1912.

¹Jour. Phys. Chem. 15, 489 (1911).

*This rated capacity was calculated, allowing two volts and sixty ampere hours per cell.

ically pure sodium sulphate. The anhydrous salt was used and the solution contained 10 per cent of this salt, by weight. This corresponds to $22\frac{1}{2}$ per cent of the crystallized salt if this be used. The battery was then charged in the usual way at the 8-hour rate for 53 hours.

A motor generator was used to supply the power necessary. The generator was driven by a three-phase induction motor. The power being available only from 6 a. m. to 12 p. m., an automatic device was employed for starting and stopping the experiment by opening and closing the generator circuit. The induction motor was left across the line at night. As it is customary to build up the voltage from 0 to 2,200 volts at the power-house without disconnecting the transformers from the line, the motor started easily without giving any trouble. In the morning the battery circuit had to be closed when the generator was delivering about three-fourths of the voltage required for normal running, for owing to the diffusion of the electrolyte the back electromotive force of the battery had dropped during the night. A solenoid was therefore designed to close the generator circuit at about three-fourths full load voltage on motor. At this instant the motor was running at about three-fourths full load speed, and the generator was thus delivering about three-quarters normal charging voltage. This would then start the charge at a lower rate and gradually increase the current as the polarization of the cells increased. At night when the power was turned off the solenoid was no longer energized, and the plunger dropped out, thus opening the battery circuit.

After the charge was completed, which can be judged by the total reduction of the sulphate on the inner sides of the plates, the plates were removed, dipped once in water, and replaced in battery acid of specific gravity 1.23. In order to get a capacity and efficiency test the battery was then discharged, charged, and discharged a second time. The results after this treatment are shown in Table II.

TABLE II.—EFFICIENCY AND CAPACITY TEST AFTER TREATMENT.

First discharge, output, watt hours.....	6,250
First charge, input, watt hours.....	6,820
Second discharge, output, watt hours.....	5,530
Ampere hour output, ampere hours.....	58.1
Energy efficiency, per cent.....	81.1
Energy capacity, of rated, per cent.....	88.7
Ampere hour capacity, of rated, per cent.....	96.9

The efficiency and capacity tests were made on second discharge, it being evident from the above figures that the first discharge shows the cell in an over-charged condition.

From a comparison of Tables I and II it is seen that the energy efficiency has been increased from 42.5 per cent to 81.1 per cent. The energy capacity of the battery has been increased from 48.7 to 88.7 per cent. The ampere hour capacity has been increased from 51.0 per cent to 69.9 per cent of the rated.

The battery was out of commission, for treatment, three days. This does not count the time required to take the efficiency runs as herein given.

The cost of regenerating the battery included the following items:

68 pounds anhydrous sodium sulphate, C. P.....	\$ 4.80
10 hours' unskilled labor at 20c.....	2.00
5 hours at 30c.....	1.50
50 kilowatt hours' power at 5c per K. W. H. (by watt hour meter).....	2.50
Total	<u>\$10.80</u>

Total cost per cell.....\$0.208
Reducing this to a commercial basis it may seem advisable to charge the loss of the use of power from the battery, while out of commission. The rated capacity of the battery is 6.24 kilowatt hours. At 48.7 per cent capacity before treatment, the capacity was, therefore, 3.04 kilowatt hours. The battery was out of commission for 54 hours, which would allow three discharges. Therefore the total power loss was $3 \times 3.04 = 9.1$ kilowatt hours. Estimated at 5 cents per kilowatt hour, this represents a loss of 46 cents. This would raise the total cost of the regeneration to \$11.26, or an increase of nine-tenths of a cent per cell.

The increase in efficiency represents a gain in output of 2.5 kilowatt hours per discharge at the normal rate of charge. At 5 cents per kilowatt hour this totals $12\frac{1}{2}$ cents. The total cost of the experiment was \$11.26. Dividing this by $12\frac{1}{2}$ cents gives 90. This means in 90 charges and discharges the saving of power, due to the increased efficiency, would pay for the regeneration of the cells.

The storage battery concerns claim that the same results can be obtained by prolonged charging at half the normal rate. This is no doubt true for cells that are not badly sulphated. While no direct measurements have been made along these lines, indications from observations in this laboratory point to the fact that a battery would have to be out of commission from three to four times as long as that required by the above outlined sulphate method. It has also been noticed that prolonged charging causes excessive shedding of the active mass and hence its total loss.

The conclusions drawn from this experiment may be summed up as follows:

1. Badly sulphated cells can be economically regenerated by electrolysis in sodium sulphate solution.
2. The cost need not be greater than 20 cents per cell.
3. Allowing 5 cents per kilowatt hour for power, the increase in the efficiency of the cell will pay for the regeneration in about 90 charges and discharges, or in about 3 months' daily use.

The estimated receipts from the Russian Government spirit monopoly for 1912 are \$365,961,000—more than a quarter of the total national revenue. The returns of the Moscow excise department show that the consumption of vodka in the Moscow Government in 1911 was 5,288,045 vedros (a vedro equals about 2.7 gals.), or 421,446 vedros more than in 1910. The consumption in this Government since July, 1901, has amounted to 57,442,936 vedros.

METALLURGY

CHILEAN NITRATE DEPOSITS.*

By E. W. McMULLEN.

The production of nitrate in Chile during the last year was valued at \$100,000,000, of which the United States consumed \$20,000,000 worth. This is about the same amount that Germany gets from the United States for potash. The mining of nitrate is the largest mining industry on the South American continent, and will probably remain so for some time to come.

The nitrate beds begin at about 19° south latitude and extend southward for about 500 miles along the west coast. They are not entirely continuous, but exist in patches with areas of material too low to work scattered through them. The northern fields or "pampas" are the best known to the author, and are described by him, although others are more or less similar.

The deposits generally occupy a comparatively narrow strip; in some places they are only a few hundred yards wide, in other places a mile and again three, four or five miles wide. The country in which they occur is an extremely arid portion of the west coast. It is 15 to 20 miles inland behind a high plateau of 4,000 to 5,000 ft. elevation, and the coast range, some 2,000 feet higher. The west side of this interior valley on the foothills of the coast range is where the nitrate beds occur. The lower portion of the valley, which is quite flat, often contains heavy salt deposits, but no nitrate.

It seldom rains in this district, but is very foggy. These fogs drift over the coast range and across the "pampas" so that while there is practically no rain the surface of the ground often becomes quite wet. It has been said that at some seasons of the year there is a great deal of static electricity in the air which might fix the nitrogen and that this might be carried down by the fog and deposited. This would probably make the richest nitrate at the surface of the ground, which is not the case.

The rocks forming the coast range are both sedimentary and igneous; the sedimentaries are generally considerably metamorphosed. The deposits themselves are rather queer in their occurrence and one could often walk over them for miles, if they were not pointed out, without recognizing the presence of anything valuable. The nitrate rock occurs usually as a brown or gray deposit in the impure state; where it is pure, it is white or pink and resembles salt. Ordinarily,

however, the "caliche," the name given to the bed that is mined, is composed of pebbles, sand or angular debris firmly bound together by the salt which has infiltrated, forming a hard conglomerate. If you examine the caliche, you will notice often that the pebbles or rock fragments are entirely separated one from the other, having been forced apart by the deposition of the nitrate. It is apparent that the material was carried into the original loose surface materials in solution and deposited, probably due to evaporation. It seems probable that the solutions were brought in by capillary attraction and that the salt was deposited much as our alkalis are formed in the west.

The deposits are always very close to the surface. Usually there is two or three inches of dust and sand over the surface. Then there will be from one to four feet of low grade caliche, carrying from 5 to 12 per cent of sodium nitrate; below that comes one to five feet of higher grade material, running from 18 to 25, and sometimes as high as 50 to 60 per cent of nitrate. The ordinary grade that is mined is 20 to 30 per cent. The bed rock below the deposit consists of shale or limestone or any rock which may have outcropped there. It is very deep and has been drilled for 600 feet without finding any nitrate. Of course the nitrate will be in the interstices of the rock debris and in the joints and bedding planes of the upturned rocks. But as a general rule the line of demarcation is distinct.

The mining method is a very simple one; it is an open-cut process in which the faces are carried forward in more or less regular lines, while the waste material is stacked up on the worked out areas. Holes 6 inches in diameter are drilled by hand to the bottom of the caliche at intervals of 30 to 40 feet in the front of the working faces. Several sacks of low grade black powder made at the mines (sodium nitrate, sulphur and coal) are put down. The blast shatters the deposit so that the pieces can be broken up by hand hammers and hand picked. The workable rock is loaded into carts and hauled to the works or ore trains, while the lower grade (below 15 per cent) is left on the ground. The loss of workable rock due to this crude method would probably be from 15 to 25 per cent.

In the nitrate works or "officinas," the coarse hand-picked rock is run through crushers and crushed coarse. The size from these crushers will vary from one to three or four inches in diameter, and is charged into the bleaching vats. These vats are about 6 feet wide, 8 feet deep and 15 to 30 feet long; they contain a coil of steam pipes going around the bottom and extending 5 feet up from the bottom. There is also

*Compiled from paper by Prof. J. E. Newsom before Mining and Metallurgical Society of America, and discussion following.

a false bottom in the tank. The solution from previous extractions is run onto the rock, heated to boiling by the steam pipes, allowed to boil three or four hours until it reaches a certain degree of saturation, when it is drawn off into the precipitation vats. A second less concentrated solution is next used and a third and fourth wash each decreasing in strength so that the last one almost completely extracts the soluble salts. The vats are run in series of four or six so that the strongest solution passes over the fresh rock and the weakest solution over the spent rock to make the evaporation as small as possible. The strong solution is allowed to stand four or five days when the sodium nitrate precipitates out as a white or brownish white salt. If it carries less than 95 per cent NaNO_3 , a penalty is attached in the market.

The chief impurity is common salt, as all the deposits contain a good deal of sodium chloride. The key to the process of extraction lies in the fact that hot water will not hold much more common salt in solution than cold water, but will hold much more sodium nitrate than cold water. When the hot and saturated solution of sodium nitrate is allowed to cool, the sodium nitrate crystallizes out while the salt remains in solution. This solution is used again until it becomes too impure for further use.

The solubility of the nitrate of soda varies greatly on account of the different combinations of other salts present in the caliche. While at ordinary temperatures 85 parts of nitrate dissolve in 100 parts of water, the solubility in the presence of sodium chloride lowers to 53 parts, dissolving at the same time 26 parts of the chloride. At 120°C ., 100 parts of water dissolve 220 parts of nitrate, while the amount of chloride in solution is reduced to 15 parts. Sodium sulphate and other salts exert a similar influence, although not as great.

When the sun and atmosphere have completely dried the nitrate, it varies between the following compositions:

Component Parts—	Per cent.	Per cent.
Nitrate of soda.....	94.164	94.245
Nitrate of potassium.....	1.763	1.249
Chloride of sodium.....	.933	1.180
Iodate of sodium.....	.010	.017
Perchlorate of potassium.....	.282	.239
Sulphate of magnesium.....	.219	.303
Chloride of magnesium.....	.289	.342
Sulphate of calcium.....	.102	.041
Insolubles.....	.138	.174
Moisture.....	2.100	2.210
	100.000	100.000

The waste material, called ripio, after having been leached, is shoveled from the vats by hand as very few labor-saving devices are used. This is piled on waste heaps and usually is of no further value. These tailings generally contain 5 to 8 per cent of sodium nitrate which is about 25 per cent of the original amount of nitrate. These piles become hard on standing, but if as in some of the older piles, they still run above 14 per cent, they may be easily broken up and again extracted. This has been done in some cases.

The precipitated nitrate is shoveled out on to drying floors, allowed to dry for several days, then sacked and shipped to the coast by rail. The export is chiefly on sailing vessels, which take it to all parts of the world.

The cost of production is very small; the principal item is the government tax of about 50 cents for 100 pounds on all the nitrate exported. This tax forms the principal revenue of the Chilean government. The output in 1911 was about 2,400,000 long tons of nitrate obtained from about 16,000,000 tons of raw material. The average price was about 7 shillings per 100 pounds, including the 2 shilling government tax.

A number of theories are advanced as to the origin of the nitrate deposits. One is that the inland basin was originally an inland sea; that it evaporated, and that the nitrate is the residue which has collected along the rim of this sea. One objection to this theory, as applied to the "Tamungal" pampa, one of the greatest of the nitrate pampas, and one which has the appearance of an old dried up lake bed, is that the nitrate deposits are only found on one of its sides, namely, the west side. If the deposits were formed by the drying of a body of water, they would certainly have been formed around the entire margin of that body. They occur on the west side towards the coast and not on the Andean side.

Another theory that has been advanced is that at the time the land was lower and formed the Pacific coast shore line; the sea birds, of which there are a number along the coast, formed guano deposits, and that these deposits were afterwards dissolved and re-deposited in their present form.

Another theory is that the deposits have been formed by winds blowing guano from the coast, over the coast range and depositing it along this eastern slope where it remained.

Another theory is a bacteriological one. It is that the nitrate of soda was deposited by bacteria in the same way that nitrogen is deposited on the roots of clover, alfalfa and other legumes. With the exception of that existing on the pampas owing to the exploitations of the nitrates, those pampas are absolutely devoid of any life of any kind, and it is difficult to reconcile this condition with the idea of bacteria forming these enormous deposits.

In going over nitrate fields I was impressed with the fact that they occur in the neighborhood of very extensive volcanic regions; some of the volcanoes are active at present, and they have all been active up to no very distant period, geologically speaking. Up in the Andes, along the portion of the range where the nitrates occur, there are extensive deposits of borax. These, in all probability, came from volcanic emanations, or the leaching of volcanic rocks, and it occurs to me that the original source of the sodium nitrates may have been in the gases emanating from the volcanoes, or in the volcanic rocks of the west range of the Andes, and that the nitrates, being very soluble, may have been carried down to the pampas by the

water passing down the west slope of the Andes, either surface or underground.

There is little doubt that the nitrates were carried to their present position in solution; that these solutions were brought near to the surface by capillary attractions, and that the nitrates were deposited owing to evaporation of the solutions near the surface. Considerable migration of the material could be brought about in this way. The difficult thing to understand, however, is the original source of the nitrate. That this source was the volcanoes of the west range of the Andes seems to me likely.

One objection to this idea is found in the fact that on the largest one of the nitrate fields thus far worked, the deposits occur on the edge of the plain farthest from the Andes. It is possible, however, that underground waters coming down from a high range would have prevented the formation of deposits at the foot of the mountain.

Much work would have to be done, and data collected relative to the composition of the rocks, volcanic emanations, and waters of the west range of the Andes, to prove or disprove the hypothesis outlined. Thus far the origin of the deposits has not been satisfactorily solved. It is an important problem and one which will take much careful work to solve.

There is one fact that raises a good deal of hope of our finding nitrates in some of our country in the west; that is, one might walk over and examine carelessly any quantity of it without dreaming of the presence of nitrates. If a prospector's attention were called to the material at all, he would probably break a piece with a hammer, taste it, and call it salt without further question. Usually salt is mixed with it, and usually there is not enough excess nitrate to detect the difference in taste. The richer rock, if powdered and sprinkled on tinder, or a live coal will burn rapidly and those working on the deposits get so that they can tell very closely the grade of the rock by that simple test.

The Chilean government have no geological survey work going on. They have a department in charge of the nitrate business; they examine the various fields and keep well ahead of the development. They have at least 100 years supply on hand, of which they know, but make no effort to have a systematic geological study.

Preliminary statistics, based upon direct returns from mine and smelter operators but subject to final revision, show the total value of Canada's mineral production in 1911 to have been \$102,291,686, a falling off of 4 per cent from the value in 1910.

The total production of the Butte district in February was in the vicinity of 28,950,000 lbs. of copper, of which the Anaconda Co. is credited with 27,450,000 lbs., compared with 26,350,000 lbs. in January.

FURNACE ELECTRODES PRACTICALLY CONSIDERED.*

By R. TURNBULL.

A number of papers have been read at the various meetings of this society during the last two or three years, and articles published in the technical papers, on electrode losses, but, so far as I am aware, the practical end of the electrode question has never been taken up by any one of our members except in a very superficial manner.

It therefore occurred to me that as electric furnace practice is only confined to a very small percentage of the members of this society, and as there must be quite a number who have never encountered electrode troubles, and who may not understand what benefit the society is getting from the above mentioned discussion on electrode losses, that for these reasons a practical paper written on the subject of electrodes by one who has been in the business for a number of years might prove of some benefit to the members as a whole.

Before going into the history of the electrode, let us first see what relation it has to the electric furnace. Putting it in its simplest form, the electrode is to the electric furnace what the steam pipe is to the steam engine. In the latter case the steam or source of energy is carried to the engine in the pipe at a certain pressure, represented by pounds per square inch and the volume of steam by the number of cubic feet. To get more power, should the volume be increased the pipe must be made larger in diameter, in order to avoid frictional losses, etc. The same result could be attained, within a certain limit, by increasing the pressure and allowing the volume to remain the same. In the case of the electrode, the pressure and volume of the steam are replaced by volts and amperes; an electrode, if large enough, will carry to the furnace a certain number of amperes with very little loss in volts, but as the amperes increase, the section of the electrode must also be increased, otherwise the loss in volts by resistance in the electrode will become serious and considerably decrease the output of the furnace. As in the case of the steam pipe, the pressure in volts might be increased in order to get more power into the furnace, but electric furnace operation is generally controlled by the voltage, and a variation from the usual number of volts would upset the good operation of the furnace.

Now let us examine what an electrode is composed of, and what constitutes a good and a bad electrode.¹ The mixture used in the manufacture of the ordinary electrode is anything but a complicated one, being simply some kind of carbon mixed with certain percentages of pitch and tar. This, after being well mixed together, is moulded in some special apparatus to the desired form, and then baked in a furnace in a non-

*Paper presented at the 21st General Meeting of the American Electrochemical Society, in Boston, Mass., April 18-20, 1912.

¹There are two classes of electrodes, the amorphous carbon and the graphite; it is the former to which I wish to draw attention, as graphite is prohibitive for ordinary furnace practice, owing to its high cost.

oxidizing atmosphere. This looks simple, and when one looks back on the troubles and tribulations experienced by technical men in electric furnace work over quite a number of years, due mainly to bad electrodes, it seems strange that the secret of making electrodes which would not break was not discovered long ago. But good electrodes were made from the very beginning, and it is quite possible that amongst the first batch of electrodes made some were equal in quality to the best electrodes made at the present day. This was where the great difficulty confronting the manufacturer lay, in his ability to, unintentionally, turn out a first-class electrode and a thoroughly bad one at the same time and under exactly the same conditions. Electrodes made at the same time, under the same conditions, and baked in the same furnace, have shown in actual service as many different characteristics in quality as could well be imagined, some giving excellent service whilst others simply went to pieces after being in operation for a few minutes.

As the electrode is to the electric furnace what the gasoline motor is to the aeroplane, one can well imagine what a bad electrode meant to the operator of the electric furnace; without the efficient gasoline engine the aeroplane would probably be unknown, and the same might be said would be the case of the electric furnace without good electrodes.

In the early stages of electrode manufacture petroleum coke was mostly employed, it being first of all calcined to drive off all volatile matter. This was afterwards replaced by retort carbon, a kind of coke which is deposited in the retorts in gas works, and which is nearly pure carbon. Better results were obtained by the use of retort carbon than with petroleum coke, and it was considered for a time the only material with which a reasonably good electrode could be turned out. I have not sufficient data to enable me to say when and where the first large electrodes were made, but I should not be far wrong in saying that they were first made by Dr. P. Héroult at his works in Froges, France, some fifteen years ago; at that time he made them as large as 16 in. (40 cm.) square and 6 ft. (1.8 m.) long. Some of these first electrodes manufactured by him were very good, and some very bad, and little if any reliable data could be collected from his work. I should like to say here, however, that Dr. Héroult has not abandoned the field, he having established works in Niagara Falls, N. Y., where excellent electrodes are now being turned out, and although the process used is different in some respects from his original one, he is still working along the same lines. His original process is still being used with good results at Welland, Ontario, by Electro-Metals, Limited.

Now, what was the reason of so many failures to turn out a good article in the early days, and why do nearly all electrode manufacturers, even those who have been but a short time in the business, turn out today a fairly satisfactory article? I think I am not far wrong in saying that the main cause of failure

was in the use of the wrong carbon material. Petroleum coke did not work well, and electrodes made from it crumbled to pieces in the furnaces. Retort carbon made a better electrode, but as this commodity was collected from gas works all over the world, a homogeneous article could not be counted upon, and this made its use dangerous to the manufacturer, so far as reliability was concerned. It was only when anthracite coal came into use that real progress was made, and the best kind of electrodes in use today are made from this material. Hardmuth, of Venisseux, France, was, if I am not mistaken, the first one to use anthracite coal on a large scale, and for some time his electrodes were the best in the market. He was quickly followed by the German makers, the Plania Werke and Siemens. We are indebted today to the Plania Werke for the moulded screw, which enables electrodes to be joined together, thus doing away with the stub and machining of the electrode and the trouble of changing electrodes in the furnace. This screwed electrode applies mainly to furnaces for the manufacture and refining of steel. At the present time nearly all manufacturers are using anthracite coal as the carbon base, and while electrodes made by some manufacturers are superior to those made by others, this is mainly due to the different methods of moulding the electrodes and preparing the coal employed.

So much progress has been made in this industry in the last two or three years that perfectly satisfactory electrodes up to 24 in. (60 cm.) in diameter and 7 ft. (2.1 m.) long are now being made, whilst only a few years ago nothing over 12 in. (30 cm.) square and 5 ft. (1.5 m.) long was satisfactory. No doubt still larger electrodes can and will be built, as electric furnaces are still growing in size, and the time is not far distant when steel furnaces of 30 tons' capacity, and operating with electrodes 3 ft. (0.9 m.) in diameter, will be as common as are our small 5-ton furnaces of today.

Before closing this paper, I would like to give a few hints as to the best manner of employing an electrode in order to ensure the best service and avoid the losses of which we have heard so much. Carbon, unlike metals, is a better conductor hot than cold, and the hotter it is, the better conductor it becomes. Carbon, however, even at a very high heat, is still a poor conductor, and it is impossible in actual practice to avoid some loss in the electrode itself. In all conductors, the longer the conductor, the greater the loss, but this loss can be lessened by increasing the size of the conductor. This same rule applies to electrodes, and in order to avoid all losses to the greatest extent possible the current should enter the electrode at a point as near as possible to the point where it will leave it. It is quite common practice to connect the metallic conductor to the head of the electrode, but this is a grave mistake, as the loss in volts in a long electrode will be from 4 to 6, depending on the current density employed, and in a furnace where the operating voltage

is 50 volts, this loss would be equal to from 8 to 12 per cent of the total energy consumed. Electrodes should be held in the same manner as one would hold a bar vertically in the hand, so that they can be taken at any point on their length, and in smelting furnaces the holder giving contact to the electrode should not be at any time more than 1 ft. (30 cm.) above the charge. As the electrode wears away it is slipped through the holder, and the process goes on until it is finally taken by the head, but at no time should the part of the electrode carrying the current project more than 2 to 6 in. (5 to 15 cm.) from the holder itself. The losses, both of heat and energy, can be decreased by increasing the size of the electrode, but this can be carried too far. The writer would recommend a current density of from 30 to 35 amperes to the square inch of section (5 to 6 per sq. cm.) in order to keep the electrode as cool as possible and thereby prevent side oxidation and heat losses. With too large an electrode, quite a good percentage of the total energy supplied to the furnace would be required to keep the electrode warm.

An important point, the value of which is sometimes overlooked when considering the size of electrodes is that it is often advisable to use electrodes of greater cross-section than electrical necessity demands, but for a totally different reason. In some processes, for instance, the electrode when working is surrounded to a certain depth by charge mixture. At the surface of such charge mixture, and therefore at some distance from the working end of the electrode, inflammable gases are given off, and these burning in air tend to attack and consume the electrode. Thus there is a tendency to reduced cross-section at this point with consequent increased current density, followed by rise of temperature, which further aggravates the condition described. It is, therefore, wise for convenience sake, to use a larger cross-section so that the burning away does not result in eating the electrode through, letting a large piece of electrode into the charge and disturbing conditions generally. This is one of the exigencies imposed by practice.

According to the London Financial Times it is reported that an amalgamation is contemplated between the Diesel Engine Co.; Carels Bros., a Belgian undertaking that manufactures Diesel engines; and Davey Paxton & Co., of Colchester. The capital of the combined undertaking is placed at £750,000 (3,650,000), of which between £400,000 (\$1,947,000) and £500,000 (\$2,433,000) may be publicly issued, and the balance held in reserve. Considerable developments are reported in connection with the Diesel engine, and this amalgamation is probably for the purpose of assisting these. The system of giving other firms a license to manufacture Diesel engines, however, has proved successful and is not to be discontinued.

ON THE NATURE OF ZINC CEMENTIZING (SHERARDIZING).*

By ARDEN R. JOHNSON, PH. D., and WILLIS R. WOOLRICH, B. S.

It is now about a decade since Sherard Cowper-Coles made the discovery, quite by accident, that if a piece of metal, like iron, for example, is buried in zinc-dust, and the mass heated out of contact with air, there is deposited on the iron a beautiful coat of zinc. The process was given the trade name "Sherardizing," but a term more appropriate, in the light of the nature of the process, is "zinc cementizing," analogous to carbon cementizing of iron.

While the commercial application of the process appears to have been slow at first, it, nevertheless, grew steadily in favor for certain kinds of goods, and, after getting a firm hold in England, appears to be spreading rapidly in the United States.

The close attention which this process is attracting may be due largely to the simplicity of the process and to the mystery surrounding the actual nature of the deposition, but, as we believe, is due more largely to the very great value of the coating as a protective agent for iron and steel goods. Any process that brings engineers and chemists one step nearer the solution of this so important problem in the realm of the conservation of building materials must surely attract the most serious attention. With this fact in mind, we present some results gleaned from a rather broad industrial research on zinc cementizing, which we hope are of sufficient scientific value to be of general interest.

Fundamental Factors in the Process.—In working the process of "Sherardizing," whether for commercial or scientific ends, we must know the amount of zinc deposit as a function of the following factors: Temperature, time, concentration of zinc-dust in inert powder, and size of zinc particles. No doubt, much of such information has been obtained, but it does not appear to have been published as definite data.

To study the effects of the above-mentioned factors, we first used a small apparatus modeled after the commercial apparatus. A piece of 2-inch (5 cm.) gas pipe about 8 inches (20 cm.) long had fitted to each end a cap. One of these caps had a $\frac{3}{8}$ -in. (1 cm.) hole bored at its center through which a thermometer could be inserted along the axis of the pipe. The other cap had drilled in it ten holes of $\frac{3}{16}$ -in. (0.5 cm.) diameter. This tube was filled with zinc-dust, or mixture, and placed horizontally in an asbestos-lined iron box heated from below by Bunsen burners. Samples to be "Sherardized" were pieces of No. 9 wire, such as is used for wire nails, about 8 ins. (20 cm.) long. When the temperature of the zinc-dust was brought to the desired value, the iron wire samples could be inserted into the zinc-dust or with-

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drawn *ad libitum* through the holes in the cap. This apparatus, though to all outward appearances a well-working machine, gave too erratic results for scientific ends, so another design was gotten up which worked very successfully, and is shown in Fig. 1.

A similar piece of gas pipe, provided with a cap at one end, served as a container for NaNO_3 , or a mixture of NaNO_3 and KNO_3 kept in a state of fusion at some particular temperature by a Bunsen burner. To prevent excessive radiation, this vessel was surrounded by an asbestos jacket. The couple of a Hoskins' pyrometer was placed in the bath as shown. With this apparatus it was found feasible to maintain any temperature from 250°C. to 500°C. within limits of five degrees.

The sample of metal to be "Sherardized" was usually 75 mm. long and a little over 3 mm. in diameter (size of No. 9 wire). This sample, after being

With the apparatus shown in Fig. 1 a dozen tubes could be hung in the bath at one heating. The gases evolved could also be collected by connecting a nitrometer with one of the tubes as shown.

Determination of Zinc Deposited Per Sq. Cm. of Surface.—The most essential and critical point to be determined under a specified set of conditions is the weight of the zinc deposit per sq. cm. Two methods were used:

(1) The determination of the increase in weight of the sample by weighing it before and after the run.

(2) Measuring the amount of hydrogen evolved from the sample by the action of HCl on the zinc coat.

For carrying out the latter method a gas burette, provided with facilities for making corrections for both temperature and pressure (described in Hem-

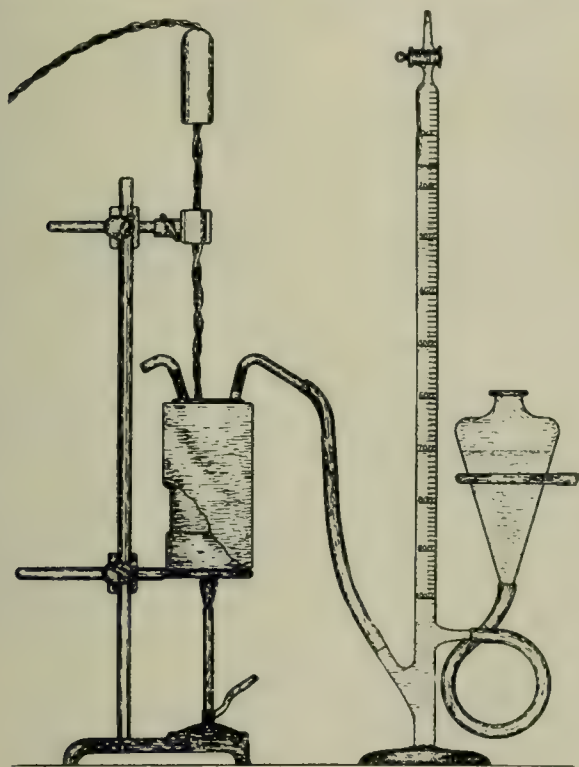
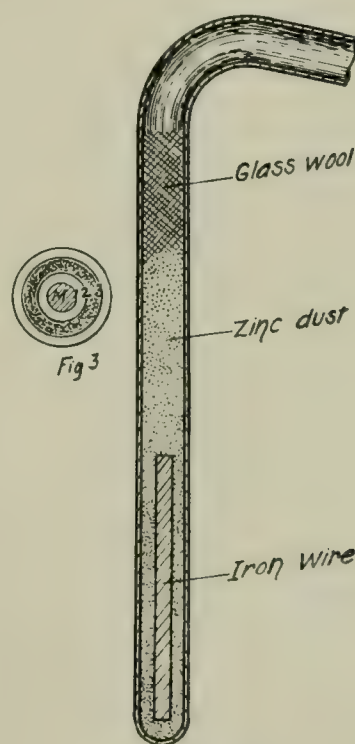


Fig. 1.

pickled, sandpapered and polished, was placed in a glass tube of about 7 mm. internal diameter, as shown in Fig. 2, and the zinc-dust, or mixture of zinc-dust and inert powder, filled in around the sample and to a considerable depth about the top of the same. A layer of glass-wool was next stuffed into the tube and gently pressed down upon the zinc-dust. The top of the tube was then heated in the Bunsen flame and given a gentle bend to a little less than a right angle with the main portion of the tube, so that the tube with its contents could be immersed in the bath with the upper end hooked over the edge of the vessel. The bend also prevented the expulsion of the glass-wool wad when the gases begin to come off rapidly from the highly heated powders. Part of the glass-wool fibers became fused to the wall of the glass tube.



Figs. 2 and 3.

pel's *Gas Analysis*, p. 73), was connected with a glass-stoppered test-tube through a side-tube on the latter. The test-tube was nearly filled with hydrochloric acid solution made by diluting one part of hydrochloric acid (*e. g.*, 1.21) with seven parts of water. Such a mixture was found to attack iron relatively slowly.

RESULTS WITH PURE ZINC-DUST.

Our first studies of "Sherardizing" were made with the purest grade of zinc-dust obtainable. The material was impalpably fine, and, under a magnification of 600 diameters, appeared to be perfectly amorphous.

Relation of Duration of Heating to Thickness of Deposit.—Several glass tubes were provided with samples of iron in the manner already described, and each one covered with approximately the same amount

of zinc-dust. The material was shaken down around the specimen by gently tapping the glass tubes on the table until there was no further appreciable settling. After carefully regulating the fused sodium nitrate bath to a certain temperature the tubes were immersed in it and maintained at constant temperature, each sample for a specified time. They were then removed, one by one, at regular intervals, allowed to cool, broken open, and, after the loose zinc-dust was wiped off with a cloth, the value of the zinc deposit was determined by one or both of the methods described.

The results of some runs are shown by the curves on Fig. 4. Curve No. 1 was obtained for polished iron at a temperature of 375°C . It is apparent that the deposition of zinc is very rapid in the first hour. After that, however, the rate is slower, and almost proportional to the time for several hours. This holds true for pure zinc-dust without admixture with an inert powder. As the first part of the curve is particularly interesting, this was studied to greater detail by preparing six samples of iron in tubes, as described, and fastening them in an asbestos holder so that they could all be immersed simultaneously in the bath, but removed singly. In the course of the heating, one tube was removed every ten minutes. Curve No. 2 expresses the results obtained by such a procedure at 420°C . It is interesting to note how rapidly and promptly the deposition starts. Also, a comparison of

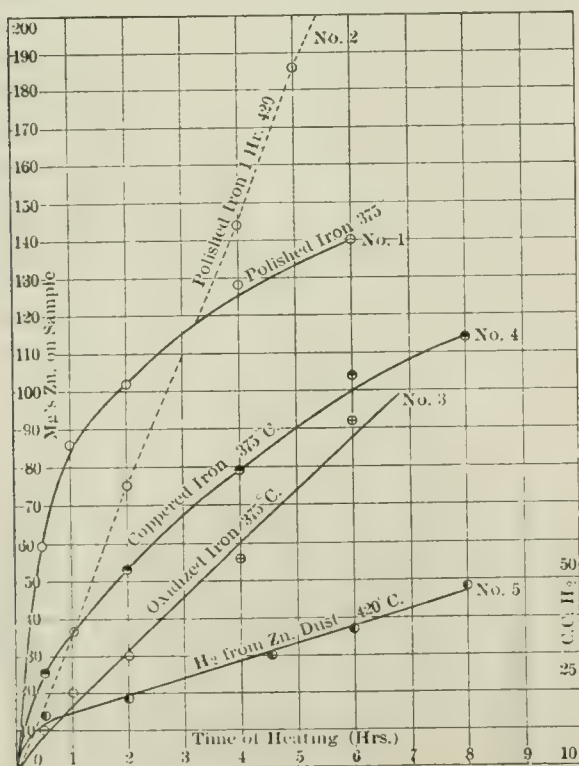


Fig. 4.

the curves for the first hour at 375° with the one at 420° shows how much higher temperature enhances the rapidity of the process.

Curve No. 3 was obtained for the same sort of iron samples as used before, excepting that they were

not pickled and polished, but left as they were—covered very uniformly with a thin film of oxide. A comparison of the curve for these rusty samples with Curve No. 1 shows what a great hindrance even a very thin coat of rust is. In fact, there was as much zinc deposited on No. 1 in one hour as on No. 2 in $6\frac{1}{2}$ hours.

Early preliminary experimentation had shown the great readiness with which copper “Sherardizes,” so a piece of iron was given a thin coat of copper and

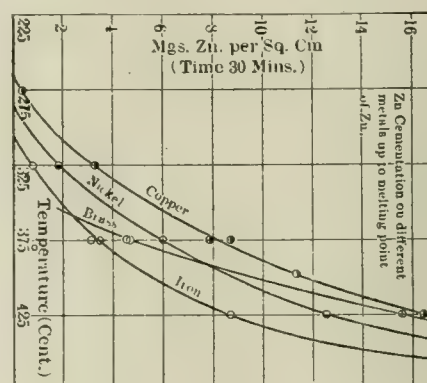


Fig. 5.

then “Sherardized” at different temperatures. Curve No. 4 would appear to show that nothing can be gained by such a procedure, though, of course, the possibilities along this line were not by any means exhausted.

Evolution of Hydrogen from Zinc-dust.—It is a well-known fact that practically all very finely-divided materials absorb and retain considerable quantities of moisture. This is notably true also of zinc-dust. With our apparatus disposed as shown in Fig. 1 we found that a very considerable volume of gas was evolved during the Sherardizing process. Curve No. 5 is a typical one, taken while “Sherardizing” samples of iron at 420°C . A qualitative examination of the gas proved it to be almost pure hydrogen, with, of course, some air. A sample of the purest zinc-dust gives up about 7 to 8 c.c. per gram, in six hours, at a temperature of 420° . This fact is quite significant, for there is thus provided a reducing atmosphere in the interstices or voids that exist in the zinc-dust surrounding the iron.

Effect of Temperature upon Rate of Deposition of Zinc.—As in most physical and chemical processes, so in the case of “Sherardizing” metals, the temperature factor is of extreme importance, and therefore many carefully arranged experiments were carried out to determine the rate of deposition of zinc not only upon iron, but also upon nickel, brass, copper and zinc. Fig. 5 shows typical curves representing the results obtained under proper conditions. Evidence is clear that not all metals, even those much less electropositive than zinc, “Sherardize” with the same degree of readiness. Copper, as might be surmised, receives a coat of zinc much more readily than the other metals. The authors have produced coats on

copper ranging from a mere film of yellow brass to a pure white of remarkable smoothness. Pure nickel "Sherardizes" more readily than iron. A rod of pure zinc, polished until perfectly smooth, did not start to "Sherardize" to any considerable extent until a few degrees below its melting point. Yellow brass receives a coat readily, but not so readily as does copper, and the curve has a somewhat different trend. But of greatest interest is the fact that all the curves approach the same rate of deposition with rise of temperature, and the limiting value lies at about the melting point of zinc. From this point on, the deposition of zinc becomes exceedingly rapid. The range of temperature between the point where the first appreciable deposit occurs to the melting point of zinc may be looked upon as the true "Sherardizing" range of temperature for a particular metal. This range is greater for copper than for iron.

Effect of State of Division of Zinc.—One of the most surprising facts which we have come upon in our study of zinc cementizing is the pronounced effect the fineness of the zinc particles has on the rate of disposition and smoothness of the zinc coat. The finer the zinc particles the smoother and apparently more penetrating the zinc coat. But the finest of zinc-dust will not deposit as fast at a particular temperature as a relatively coarse zinc-dust of 150 to 100-mesh. Results were obtained which showed nearly twice as rapid a deposition of zinc at 370°C. , in three hours, from 150 to 100-mesh zinc, than from the first zinc-

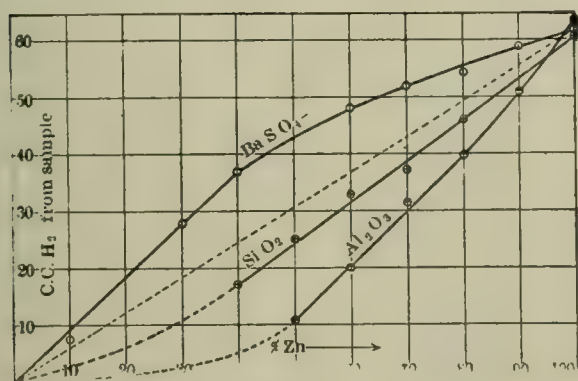


Fig. 6.

dust. The coat is quite rough for the coarser dust, however. For commercial work, one might strike a proper medium between smooth, penetrating coats, slowly deposited, on the one hand, and rough, thick coats, quickly deposited, on the other. Coarse zinc-dust is much less satisfactory in other respects when used alone than fine zinc-dust, for it yields but little hydrogen when heated, and the voids are so large as to allow air to penetrate the mass to considerable depths and oxidize both the sample receiving a coat and the particles of zinc, often to such an extent as to destroy the "Sherardizing." Besides, there is a great tendency for the coarser material to fuse together. It is therefore necessary to use some impalpably fine, inert powder with such so-called "finely divided zinc," to at least partly fill the voids.

Zinc-dust with Inert Powders.—The curves in Fig. 6 are plotted for results obtained with bauxite, barium sulfate and powdered quartz mixed in different proportions by weight with zinc-dust. These powders were exceedingly fine, and, before being mixed with zinc, were heated to 500°C. for some time to drive off moisture. With barium sulfate the deposition of zinc falls off slowly, while with quartz and bauxite the deposition falls rapidly. Reasons for these different effects are found partly in the fact that the latter powders are much more voluminous than barium sulfate, and also appear to "cake" quite readily with the lower percentages of zinc. If a powder like barium sulfate is mixed with zinc-dust by volume instead of by weight, the deposition is about proportional to the zinc content, as shown by the dotted line.

A rather surprising fact presented itself when we opened several glass tubes containing samples which had been charged with mixtures of zinc-dust and bauxite, or zinc-dust and quartz, and heated several hours. As the percentage of inert powder is increased there is a greater and greater tendency for the contents of the tube to cake. Up to 40 per cent of inert powder this congealing is not sufficient to exert much influence on the process, but greater percentages interfere with the deposition of the zinc. The contents of several tubes with only about 10, 20 and 30 per cent of inert powder, heated at 385°C. for four hours, were just sufficiently caked to barely hang together. It was noticed that immediately next to the iron sample there was a zone of considerable thickness of pure white powder; then around this another zone which was composed of zinc-dust and inert powder like the original mixture. It was also very noticeable that the demarcation between the white zone and the residual zinc-dust mixture zone was very sharply defined. Further examination under a powerful microscope revealed the fact that there was hardly a particle of zinc remaining in the white zone, and that the surface of demarcation between the two zones was really remarkably defined. The thickness of the white zone varied, of course, with the duration of run, temperature and concentration of zinc-dust mixture.

Fig. 3 represents a cross-section of the system after being heated. *M* is the iron wire sample, 1-2 is the white, pure, inert powder zone depleted of zinc-dust, 2-3 is the zone of zinc-dust and inert powder of original composition, 1 is the deposited zinc coat on the iron, 2 is the surface of demarcation between the zones described.

Theory of Zinc Cementing ("Sherardizing").—We regard the above-described experimental facts of value in determining the nature of zinc deposition in the "Sherardizing" process. Our explanation or theory of the process is as follows: In the light of the phase-rule we may regard the iron, zinc and vapor as forming a closed system, all parts of which are practically at the same temperature. Zinc, compared with iron

and most other metals, has a relatively high vapor tension. Zinc alloys fairly readily with many of the common metals like iron, nickel and copper. When the process is ready to be started, the iron, for instance, is surrounded and in intimate contact with many particles of zinc. Under the influence of heat these particles, carrying their slight atmospheres of zinc vapor, form a superficial alloy with iron. This superficial alloy on the iron would very likely be a solid solution of zinc very rich in iron. Now we may look upon the iron with its insignificant vapor pressure, as greatly lowering the very appreciable vapor pressure of the zinc which is forming a solid solution with it, and we should expect the zinc vapor to distil from the points of higher tension to the place of low vapor tension at the surface of the iron-zinc alloy. As the iron alloy grows richer and richer in zinc under the process of sublimation or distillation, its vapor tension will gradually approach the tension of the vapor of pure zinc particles, and hence the process gradually ceases.

The experimental facts already presented show that the nature of the metal to be "Sherardized," having reference to its alloying properties with zinc, has a great influence on the temperature at which "Sherardizing" will start and its rapidity after starting. That we did not succeed after several trials in depositing zinc on a pure zinc rod buried in zinc-dust is also in accord with our theory. Also, pieces of iron which had once received a coat of zinc of considerable thickness refused to "Sherardize" at any such rate as fresh iron at temperatures below the melting point of zinc. However, if the coat of zinc already present is thin, the deposition will start again, though more or less tardily.

New lines for experimentation are suggested by this theory which should at the same time test its validity. We should expect zinc cementizing to be greatly retarded if the finely-divided zinc used were a solid solution with some metal of low vapor tension, as iron, nickel or copper. If the vapor tension of the metal to be deposited is lowered until about equal to that of the most saturated solution possible on the surface of the metal being "Sherardized," the process should not take place, or only to a slight extent. Furthermore, any substance which would impair or change the initial alloying tendencies of the metals should also greatly influence the process. It is along these lines that the authors are now proceeding in their experimentation.

The Groningen Agricultural Society, in the north-eastern corner of the Amsterdam Netherland District, has approved a proposition for establishing a co-operative beet sugar factory in that section. The agricultural societies of Friesland, the next Province on the west, will be invited to assist in this enterprise. The five beet sugar factories in this consular district are now (Feb. 29) making contracts with farmers for supplies of beets during 1912. It is reported from

Friesland that the entire crop to be planted in that locality this year has already been sold at a uniform price of 13.50 florins (\$5.43) per metric ton of 2,204.6 pounds. This is a very high price, attributed to the fact that sugar beet seed costs about 30 American cents a pound this year compared with about 12 cents in 1911. According to other contracts now being made in this district, the price to be paid is 11.50 florins (\$4.62) per metric ton of beets with a sugar percentage of 14. For each one-tenth of 1 per cent more or less than 14 the price will be increased or reduced 0.10 florin (4 cents). In some cases in this locality last year a percentage as high as 17 was reported.

According to the preliminary report of the Department of Mines of the Dominion of Canada the smelter production in Canada in 1911 for which complete returns were received with the exception of one or two plants recently established for the treatment of Ontario silver cobalt ores was as follows: Including a small amount of imported ores, the total quantity treated in 1911 was 2,192,727 tons, as compared with 2,683,714 tons in 1910. Smelter products shipped outside of Canada for refining during 1911 were: Blister copper carrying gold and silver values, 10,710 tons; copper matte carrying gold and silver values, 11,320 tons; Bessemer nickel copper matte, carrying small gold and silver values as well as metals of the platinum group, 32,607 tons. Of the gold production \$4,580,000 is credited to the Yukon placers, as against \$4,550,000 in 1910, the total exports on which royalty was paid being 277,430.97 ounces in 1911, and 275,472.51 ounces in 1910. Returns of the silver production indicate a falling off of about 128,516 ounces; the total for the year is estimated at 32,740,748 ounces, of which 30,761,690 ounces were from Ontario, 1,910,323 ounces from British Columbia, 50,300 from the Yukon, and 18,435 ounces from Quebec. Shipments of ore and concentrates from the Cobalt district and adjacent mines aggregated 16,234 tons, containing approximately 28,817,198 ounces, in addition to which 3,334,052 ounces were shipped as bullion. The average silver content of ore and concentrates shipped was thus about 1,744 ounces or \$929.62 per ton, as compared with an average of 867 ounces in 1910 and 840 ounces in 1909. There is practically no production of refined copper in Canada, and the output is represented by the copper contents of smelter products, together with the amount of copper contained in ores exported estimated as recoverable. The total production on this basis in 1911 was 55,848,665 pounds, as compared with 55,692,369 pounds in 1910. The total copper contents of ores shipped in 1911 was approximately 67,282,590 pounds, being 3,123,189 pounds from Quebec, 21,402,221 pounds from Ontario, and 42,757,180 pounds from British Columbia. This record is of special interest as illustrating the distinction between ore contents and smelter recoveries.

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HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

Protection and the Patent Laws.

The United States is practically the only industrial country in the world which does not require the manufacture within its territory of articles protected by patent laws. We alone of all nations issue patents to foreign citizens, giving them a complete monopoly of our market; permit them to manufacture the patent article where they please and then put a high tariff on the article. This tariff does not protect American industry, because the patent issued to foreign citizens prevents the manufacture of the article here unless the patentee sees fit to start a factory. If made abroad, the manufacturer adds the duty to the price he wishes to realize from his patented article.

This policy affects injuriously many lines of industry, chemical compounds being probably the hardest hit. Between 1900 and 1910 the United States issued 340,000 patents, an average of 30,910 a year, and of these 38,930 that is 11.4 per cent, or 3,540 each year were issued to citizens of foreign countries, the patentees and their assignees living in foreign countries.

The American market is the most valuable market in the world, and to grant a foreigner a monopoly of it without asking any return whatever is industrial suicide. To provide in addition for an import duty on articles which by our own laws we have prevented ourselves from manufacturing is unspeakably idiotic.

Up to 1907 the English patent laws did not require compulsory working in England of patents issued there, but in that year a compulsory working amendment was added to the patent laws. The London Times in its issue of March 23, 1911, states that the operation of the law has had the effect of compelling 50 foreign firms to establish plants in England, involving an investment of \$4,000,000, the employment of 7,000 wage earners, and a weekly payroll of \$40,000.

France, Germany, England and many other countries require the manufacture of any patented article in the country granting the patent, within one year of its issue, on penalty of a forfeiture of the patent.

Our patent laws should be amended without delay to cover the compulsory working of the patent under the flag of the United States within a specified time. In other words, a patent should be a license to be the sole manufacture in America of the article covered by patent, not the sole vender, regardless of the place of manufacture.

Regulations for Illuminating Gas.

Chemists and engineers connected with the manufacture, testing or regulations governing the sale of illuminating gas will welcome a circular recently prepared by the National Bureau of Standards. This circular has been prepared after conference and correspondence with a large number of gas engineers and inspectors; and it represents, as nearly as possible, the average opinion of many men active in the field of gas manufacture and gas testing.

Part I of the circular gives a summary of the municipal gas ordinances now operative, presents a general discussion of municipal gas requirements, and proposes an ordinance largely compiled from the best ordinance requirements now in force.

Part III quotes a few ordinances typical of those recently enacted and gives the main portions of state gas laws now in force affecting gas quality, pressure and meter accuracy.

The circular does not concern itself with financial regulation of gas companies nor does it include any discussion of the comparative value of various methods of works management. It deals mainly with the candle power, heating value, purity and pressure of the gas and gas meter testing.

The present publication has grown out of the investigation of the methods and standards employed in gas photometry and gas calorimetry, undertaken by the bureau three years ago. A second circular on the methods of testing employed for official inspection work is now being prepared. Although it cannot be expected that the regulations for or methods of gas testing will ever be entirely uniform throughout the country, it is believed that if the results of a comprehensive investigation of the subject are published, a greater uniformity of method, and in some cases more accurate measurements will result.

The attitude of the Bureau of Standards is entirely advisory and its intention is to place in the hands of

the technical and general public an impartial and, as nearly as may be, an accurate summary of the facts which must be considered in connection with the fixing of standards of quality and the testing of illuminating gas.

Revision of the circular from time to time is contemplated in order to amend the recommendations as to the requirements to adapt it to new developments in the gas industry.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of patents, McGill Building, Washington, D. C.

1,016,293. **Decaffeinated Coffee.** Nathan Rosewater, Cleveland, Ohio. Patented February 6, 1912.

1,016,352. **Phosphate** and the Method of Making Same. Charles Nicholas Meriwether, Clarksville, Tennessee. Patented February 6, 1912.

1,016,407. **Process for Hardening and Water Proofing Animal Skins.** Karl Hartmann, Berlin, Germany. Patented February 6, 1912.

The process consists in hardening and waterproofing animal skins, after removal of hair and flesh, by treating them in a bath of amyl acetate and acetone, then applying to the skin a solution of celluloid in amyl acetate and acetone, and then treating same in an alcoholic solution of shellac.

1,016,445. **Paint and Varnish Remover.** Christian M. Edward Schroeder, New York, N. Y. Patented February 6, 1912.

1,016,476. **Purification of Gasses.** Frederick Gardner Cottrell, Berkeley, Cal., assignor to International Precipitation Company, San Francisco, Cal., a corporation of California. Patented February 6, 1912.

1,016,548. **Milk Product** and Process. Charles H. Campbell, New York, N. Y., and Pearl T. Campbell, Hackensack, N. J. Patented February 6, 1912.

1,016,549. **Iron-Nichol-Copper Alloy.** Gulliam H. Clamer, Philadelphia, Pa. Patented February 6, 1912.

1,016,761. **Process of Producing Starch and Glucose.** Charles C. Moore, Lexington, Ky. Patented February 6, 1912.

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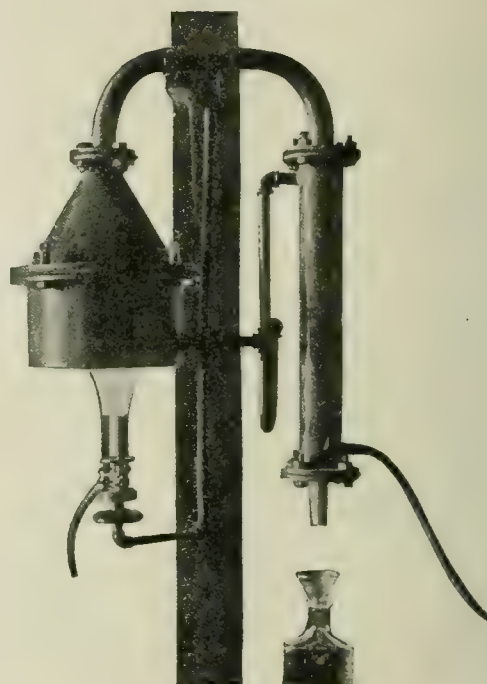
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CHICAGO, MAY, 1912.

No. 5.

THE RECENT DEVELOPMENT OF PEAT AS A POWER FACTOR.*

By DR. T. A. MIGHILL.

So new is the use of peat as a fuel for power purposes, that the whole development of the industry has taken place in less than a decade, and the greater part of it in less than five years. With this introduction, and no apology on account of the title, I propose, in this paper, to state what has been accomplished from what information I have been able to obtain.

Peat has been burned under boilers, distilled in retorts, and gasified in producers. It has been used as dried turfs, machined blocks, briquettes and dust. It has been used with a content of water varying from 10 per cent to 60 per cent. The countries of Sweden, Germany and Great Britain have taken the lead in the development of peat power. As early as 1872 peat was gasified for metallurgical purposes at the Moltala Iron Works in Sweden. In 1903 a small plant was erected at Skabersjö for power purposes. The Körting machinery was installed and the capacity of the plant was about 300 h. p. A 60 h. p. plant was erected at Burangsberg. In 1907 one of 1,000 h. p. was projected at Wisby and a smaller one at Sunne. In 1909 Consul Murphy reported the erection of a central power station at Svedala to supply electricity to neighboring towns.

In 1909 the Swedish Railways experimented on the possibilities of peat as a fuel for locomotives. Trains of about fifty cars were run twice daily and 140 trips were made. The cost of prepared peat was reported to be \$1.84 per ton. However, the managers were not convinced of the practicability of using peat fuel and the director ordered the tests discontinued.

One of the latest developments in Sweden is the preparation of peat powder as a fuel. An experimental plant was established at Bäck. The peat was machined, formed into bricks and air-dried, then crushed between rollers provided with toothed rings, further crushed between discs provided with iron pegs and then bolted and dried. 1.2—1.4 tons of this powder are reported to be equal to one ton of coal. The cost

per ton as fired was nearly equal to the cost of coal as evinced by the trials, as some coal had to be used, the ratio being as \$3.25 to \$3.95. Dr. Ekelund has a process of preparing peat powder. The details are not yet available. It is said that he air-dries the peat, then lets it be exposed over winter. It is thereby more easily pulverized and less hygroscopic.

Russia is a great peat country. In central Russia in 1908 there were seventy-three firms making peat fuel with a total of 960,000 tons, according to Consul De Soto. The average cost was \$1.40 not delivered. Notwithstanding, no noteworthy development of the use of peat as a source of power has taken place.

Ireland has been noted for its peat deposits, peat having been dug there for household purposes for unknown years. The development of the power proposition, however, has not been very great. In 1909 the Dublin and Central Ireland Power Co. applied to Parliament for a charter to supply the counties near Dublin with electric power generated from peat fuel. They proposed to build a plant about twenty-seven miles from Dublin in Kildare Co. and to furnish 15,000 h. p. for fifty years. The process of Ziegler was to be used. I understand that much money was spent without practical results.

At Carnlough, Woltereck erected a plant to demonstrate his process of making ammonia by running air over heated moist peat. According to the inventor more nitrogen was fixed as ammonia than was contained in the peat. His claim has been strenuously combatted by others. However, I do not understand that he intended to furnish power by his process. Last year Consul Culver reported discouragingly on the peat industry of Ireland, numerous plants being idle.

In England The Power Gas Co., the promoters of the Mond system of making producer gas, with the recovery of ammonia as a by-product, tried peat in their producer. In 1908 Dr. Caro, experimenting at the Mond Works at Soddington, gave the impetus to a most important development of the peat power problem.

In the Mond producer coal is gasified with an excess of steam at a low temperature. The nitrogen contained in the coal is nearly all fixed as ammonia which is subsequently recovered as ammonium sulphate. Dr. Caro found if peat be used as a fuel with

*From the Journal of the American Peat Society.

some 50 per cent of moisture, that by heating the air blast to 350°-550° C. almost all of the nitrogen in the peat could be fixed as ammonia.

In co-operation with Dr. Frank he had earlier developed the fixation of atmospheric nitrogen through the formation of calcium cyanamide. Together they worked out the process of fixing the nitrogen of peat in the Mond producer.

In 1897 Dr. Frank proposed the utilization of the peat bogs of Germany as a source of fuel for steam raising purposes. He proposed erecting central electric stations at the bogs which would furnish the current to neighboring towns. In 1903 he recommended the gasification of peat in producers whereby twice as much power could be obtained from a given amount of peat fuel. In 1908 Caro advocated the same procedure for Eastern Prussia.

In 1905-1906 the Mond Co. experimented with Irish peat at Stockton and with Italian peat at Winington. The Irish peat contained 1 per cent nitrogen, the Italian peat 1.6 per cent nitrogen. From the latter peat they were able to recover 120 lbs. ammonium sulphate and something over 60,000 cu. ft. of gas with heat value of 152 B. t. u. per cu. ft. from a ton of dry peat. The development of the process was now carried on in Germany with Dr. Caro at the plant of the Mt. Cenis coal mine at Soddington, Westphalia. Peat was furnished by the government and two different lots were experimented on, as much as forty tons per day being gasified. One ton of dry peat yielded over 89,000 cu. ft. of gas, with a calorific value of 158 B. t. u. per cu. ft. The plant, however, was designed to be operated on coal mine refuse and has been chiefly run on this class of fuel.

Further data on the process and character of the gas need not be given here as they are easily available. Dr. Caro has recently said if the peat contain 50-60 per cent moisture that the yield of ammonia is greater and most of the nitrogen in the peat is fixed, whereas if the straight Mond process is used it is more efficient to use much drier peat. Dr. Heber reports that he was informed by Dr. Caro, that if the peat contained 1.25 per cent nitrogen, the combined cost of preparing the fuel and gasification is covered by the sale of the ammonia and that the gas is obtained free. Further, if the nitrogen in the peat is from 2 to 2.5 per cent, that the cost of generating electric power is nothing. He has elsewhere shown that when peat is coked much of the nitrogen is retained in the coke, thus advocating the worth of his process. Dr. Caro's claims have been attacked by the Power Gas Co., giving the credit of the use of peat as a fuel in a producer with recovery of ammonia to Dr. Mond.

As a result of the experiments in England, several plants were projected in Italy and Germany. The Italian plant was erected near Pontedera, and the promoters claim very satisfactory results. It was examined by some French engineers who reported that

all of the claims of those who erected the plant were met.

A plant was erected in Germany near Osnabrück, which has hardly been proved out as yet.

It is in Germany that the greatest development of the use of peat as a source of power is taking place. This is probably due to the long experience of the Germans in making peat fuel, and to the encouragement given by the Government to cultivate the waste bog lands in the empire. Most of the bogs are owned by private parties, but some are still public property. There is an association with over a thousand members called the Verein zur Forderung der Moorkultur im Deutschen Reiche, which devotes its attention to the reclamation of bog land. They publish a magazine now in its twenty-ninth year.

The yearly production of peat in Germany is very large. Consul Teichman reports, this spring, an annual production of 11,023,120 tons.

To encourage the colonization of these bogs, it is proposed to erect central power stations which will consume the peat taken off the land as it is improved and in turn supply electrical power to the settlers and surrounding towns.

Two such plants have been erected so far, one near Osnabrück, and one near Aurich. These plants have been financed by private parties. The first thing to be done in these settlements is to dig canals to drain the bog. The peat which is removed is used as fuel in the central station, and so far has constituted practically the entire supply. The central station supplies power to operate the dredging machinery. Fuel is transported by trains pulled by a gasoline locomotive. Agricultural machinery has been developed which is operated by electrical power, and it is expected that the colonists will avail themselves of the power close at hand and do their farming with machinery.

The central station near Aurich is the farthest advanced. It was erected by the Siemens Schuckert Co. It is a steam plant provided with turbine engines. Dr. Kamm, Ober-Regierungsrat at Berlin, gives the following information. The total horsepower of the plant is 6,000; at present only 2,500 horsepower are available. The current is sent as far as Wilhelms-haven on one side and to Emden on the other. In 1910, 2,870 carloads of peat fuel were burned together with some coal, as the supply of peat was inadequate, but in the last five months only peat fuel was used. Six million K. W. H.s have been supplied to consumers and day and night 900 K. W. H.s to the harbor works for pumping; 6.6 lbs. of peat fuel were consumed per K. W. H., but it is expected to reduce this to 5.5 lbs. The total power developed last year was 8,000,000 K. W. H.s. Should this consumption be tripled, as seems likely, there is sufficient peat fuel available to supply the central station for 700 years.

The plant near Osnabrück was erected by the German Mond Gas Co. Its capacity is 1400 K. W. The peat fuel is gasified according to the Mond process

with recovery of ammonia. The plant is now in the testing stage, and should it prove more successful than the plant near Aurich, it is proposed to erect the same kind of a plant there.

The cost of the plant is greater than the cost of a same size steam plant, and Dr. Kamm says it consumes more fuel per K. W. H. This is offset by the value of the ammonium sulphate recovered which brings \$65.00 per ton. However, should the synthetic process of making ammonia now being developed prove successful, the whole business would be on another basis.

A year ago the Görlitz Machine Co. erected a 500 h. p. plant at Jekaterinburg, Russia, in a mill. It has run day and night and consumes 1.98 to 3 lbs. of peat fuel per h. p. h., according to the moisture content of the peat. The producers are double walled preheating the blast. The draft is divided but mostly downward. Much of the water evaporated is blown off as steam through a purging stack.

Ziegler, the inventor of the coking process, has also invented a producer for peat. A plant was erected at Schelecken using his process. It was of small size and ran an 80 h. p. engine. Afterwards the gas was used for a steel furnace. The Ziegler coking process was not intended primarily for power purposes, as the gas was used to heat the retorts. This process has not been very successful financially, the Bavarian works having been liquidated. Dr. Heber says Dr. Ziegler informed him that the cost of peat fuel and the cost of purifying the tar and tar water were excessive, prohibiting commercial success. Lately Dr. Ziegler, now with a Russian concern, has perfected a Dewaterer for peat of which details are not published, which may change the situation. The peat is pumped through a filter cell narrowed at the bottom, so that the water is pressed from a thin layer of peat. He claims to reduce the water in the peat from 90 to 70 per cent. Three other coking processes are also reported.

Other plants which have been reported are one at the Solingen mines, Westphalia, to furnish power, and one in Schleswig-Holstein, erected by the Körtings, as a central power station.

A novel process of generating power from peat was invented by Gercke. The peat is heated in a boiler. The evaporated steam is used to drive a steam engine. This was tried out practically but was abandoned for an ordinary boiler. There seems to be a sharp rivalry between the promoters of the suction producer and the promoters of the by-products recovery producer. One writer representing the Görlitz people has claimed greater efficiency for the suction producer, using the power to fix the nitrogen of the air as calcium cyanamide. Dr. Caro objects to this, claiming a misunderstanding of figures, that the Mond process gives ammonia directly, and that the other process demands the previous preparation of calcium carbide. Moreover, the ammonia in the form

of sulphate, is immediately available, which is not the case with cyanamide. However, the Mond process does not apply to plants with less than 1,000 h. p. Which side has the better argument is not yet clear, and it may be said that in 1904 Dr. Frank advocated the use of peat fuel to make carbide. According to Dr. Kamm, from whom I have drawn information about the central stations in Germany, it is not yet settled which is most profitable, direct firing of peat under boilers, burning it in suction producers, or burning it with recovery of ammonia.

Consul Teichman reports, this spring, that there has not as yet been in Germany a satisfactory solution of the problem of making gas more cheaply from peat than from coal.

Other concerns making peat producers in Europe are the Julius Pintsch Co., G. Luther, Braunschweig, and the Compagnie de Gas at Paris.

In America there has been no advance beyond the experimental stage, in using peat as a source of power. Some peat fuel manufacturers have fired their boilers with peat but only in a small way. The U. S. Geological Survey has made some tests with peat fuel and the Canadian government has a peat plant at Alfred and a producer plant with engine and generator at Ottawa.

Reports of this work are to be found in the bulletins issued by the respective governments.

Outside of these trials, several private concerns have built producers adapted to peat fuel and made experimental runs. One of the best of these runs was by the Gibbs Gas Engine Co., at Jacksonville, Florida.

In 1907 a company was formed in New York to make peat fuel and furnish power in Mexico. The plant was to be erected the next year. I have not learned the fate of the project. Col. Astor made a producer which ran a 150 h. p. engine operating a stone crusher. No figures are available.

One of the latest, but untried projects, is being exploited in Boston. The plan is to burn peat in a producer capable of withstanding some 200 lbs. pressure. It is claimed wet peat can be used. The steam generated is to be used to drive a steam engine. After the condensation of the steam the gas is to be used to drive a gas engine. The promoters do not seem to have figured much on the heat equation, fouling of the engine through tar, or the requirements of a varying load, as occurs in street railway service.

A most welcome proposition is that of the Power Gas Co. to erect a power and demonstration plant in this country. They favor Florida as a location. Their representative was here this spring looking over the situation. I spent a day with this gentleman and was much impressed with his confidence in the success of the Mond process.

In conclusion, my opinion of the peat power proposition is that the solution of the matter lies with the

peat fuel manufacturer. Until peat fuel can be made more cheaply, and in larger quantities than at present, we are not likely in America to see many peat power plants. The peat fuel manufacturer must get a more comprehensive idea of the large amount of fuel to be supplied, and that supply maintained through winter as well as through summer, and of the large drying surface required to air-dry the necessary amount of peat, even with 50 per cent of moisture in the product.

The situation in the German peat colonies is almost ideal. The farmers want to get rid of the peat. They have a market at their door as well. From the central station comes the power they need to develop their land and also ammonium sulphate and ashes as fertilizer. We are not yet compelled to move to the bog for a home and we want higher pay for our labor. I believe, as I maintained last year, that the solution of the peat power problem will come in this country only with the introduction of machinery to manufacture the fuel, to dig, spread and harvest it. I have reason to believe that this will be done both from what I have seen in the work of others and what has been accomplished at our own experimental plant.

A U. S. Consular Report states that within the last few months there has been perfected in England a method for using the fiber of the *Posidonia australis*, found in the southern seas. The report states that samples were submitted by the Board of Trade to a Manchester university demonstrator, who experimented therewith and reported that the raw fiber seemed to have fragments of sea debris among it—some seedlike objects and very minute shells, which all came away in the process—and the limp straggling fiber, after treatment, was soft, pliable, strong, much like wool in its disposition to curl and twist, and easy to spin in its raw state. It takes dye well, except with respect to green, when the result is usually cloudy. Also it requires a mild bleach, to avoid making the fiber tender. It is treated on long-fiber machines, so that the varying lengths of the *Posidonia* can be fully and fairly taken up in the sliver or roving. Woolen spinners generally spin their fiber in an oily state and afterwards get rid of the oil. In the case of the new fiber this would involve some risk of damage. It should be spun without oil. When the fiber is ready for spinning, brushing or combing is used rather than the rougher process of deviling. Brushing or combing gives immediate parallelization of the filaments, whereas deviling involves thorough breaking up and disintegration of the fiber. After the raw material has been treated for two hours, plus the time of drying, it is ready for the spinners. One man can prepare a ton a week. The manufacturers say that the estimated cost of delivery and preparation of the raw material, ready for the spinner, is 2 cts. f. o. b. and after spinning, weaving, and dyeing charges have been added the finished fabric, 52 ins. wide, can be put on the market at 12 to 14 cts. per yard.

UNITED STATES GOVERNMENT SPECIFICATIONS FOR PORTLAND CEMENT.

In June, 1911, the secretary of the Department of Commerce and Labor arranged, through the secretaries of the various departments, for a conference of government engineers for the purpose of unifying the specifications for Portland cement used by the United States government. At this conference a committee was appointed to consider existing specifications and to recommend a single specification for Portland cement to be used by all departments of the government.

After an extended series of meetings of this committee, at which careful consideration was given to representative specifications for Portland cement, as well as to all available data on methods of tests, a tentative specification was developed, which was reported to the departmental conference at a general meeting held July 20, 1911.

In view of the desirability of agreement between the specifications in use by the public and those adopted by the government, the committee was instructed by the conference to confer with representative consumers and manufacturers as well as the special committees of the national engineering societies more directly interested in the subject of cement specifications. As a result the tentative specifications first reported by the departmental committee were modified slightly, until substantial agreement was reached on practically all points except the methods of determining the normal consistency and time of setting, and the following specifications were unanimously adopted by the departmental conference at the meeting held Feb. 13, 1912.

It was recognized that no specification can be considered final, but must be subject to revision from time to time as occasion requires, and provision will be made for such revision by the various government departments, all of which have adopted the specification as recommended by the conference.

Definition—1. The cement shall be the product obtained by finely pulverizing clinker produced by calcining to incipient fusion, an intimate mixture of properly proportioned argillaceous and calcareous substances, with only such additions subsequent to calcining as may be necessary to control certain properties. Such additions shall not exceed 3 per cent, by weight, of the calcined product.

Composition—2. In the finished cement, the following limits shall not be exceeded:

	Per cent.
Loss on ignition for 15 minutes.....	4
Insoluble residue.....	1
Sulphuric anhydride (SO ₃).....	1.75
Magnesia (MgO).....	4

Specific Gravity—3. The specific gravity of the cement shall be not less than 3.10. Should the cement as received fall below this requirement, a second test may be made upon a sample heated for 30 minutes at a very dull red heat.

Fineness—4. Ninety-two per cent of the cement, by weight, shall pass through the No. 100 sieve, and 75 per cent shall pass through the No. 200 sieve.

Soundness—5. Pats of neat cement prepared and treated as hereinafter prescribed shall remain firm and hard and show no sign of distortion, checking, cracking, or disintegrating. If the cement fails to meet the prescribed steaming test, the cement may be rejected or the steaming test repeated after seven or more days, at the option of the engineer.

Time of Setting—6. The cement shall not acquire its initial set in less than 45 minutes and must have acquired its final set within 10 hours.

Tensile Strength—7. Briquettes made of neat cement, after being kept in moist air for 24 hours and the rest of the time in water, shall develop tensile strength per square inch as follows:

	Lbs.
After 7 days.....	500
After 28 days.....	600

8. Briquettes made up of 1 part cement and 3 parts standard Ottawa sand, by weight, shall develop tensile strength per square inch as follows:

	Lbs.
After 7 days.....	200
After 28 days.....	275

9. The average of the tensile strengths developed at each age by the briquettes in any set made from one sample is to be considered the strength of the sample at that age, excluding any results that are manifestly faulty.

10. The average strength of the sand mortar briquettes at 28 days shall show an increase over the average strength at 7 days.

Brand—11. Bids for furnishing cement or for doing work in which cement is to be used shall state the brand of cement proposed to be furnished and the mill at which made. The right is reserved to reject any cement which has not established itself as a high-grade Portland cement, and has not been made by the same mill for two years and given satisfaction in use for at least one year under climatic and other conditions at least equal in severity to those of the work proposed.

Packages—12. The cement shall be delivered in sacks, barrels, or other suitable packages (to be specified by the engineer), and shall be dry and free from lumps. Each package shall be plainly labeled with the name of the brand and of the manufacturer.

13. A sack of cement shall contain 94 lbs. net. A barrel shall contain 376 lbs. net. Any package that is short weight or broken or that contains damaged cement may be rejected, or accepted as a fractional package, at the option of the engineer.

Inspection—14. The cement shall be tested in accordance with the standard methods hereinafter prescribed. In general the cement will be inspected and tested after delivery, but partial or complete inspection at the mill may be called for in the specifications or contract. Tests may be made to determine the chemical composition, specific gravity, fineness, sound-

ness, time of setting, and tensile strength, and a cement may be rejected in case it fails to meet any of the specified requirements. An agent of the contractor may be present at the making of the tests or they may be repeated in his presence.

15. In case of the failure of any of the tests, and if the contractor so desires, the engineer may, if he deem it to the interest of the United States, have any or all of the tests made or repeated by the Bureau of Standards, United States Department of Commerce and Labor, in the manner hereinafter specified, all expenses of such tests to be paid by the contractor. All such tests shall be made on samples furnished by the engineer.

STANDARD METHODS OF TESTING.

Sampling—16. The selection of the samples for testing will be left to the engineer. The number of packages sampled and the quantity to be taken from each package will depend on the importance of the work, the number of tests to be made, and the facilities for making them.

17. The samples should be so taken as to represent fairly the material, and, where conditions permit, at least 1 barrel in every 50 should be sampled. Before tests are made samples shall be passed through a sieve having 20 meshes per linear inch to remove foreign material. Samples shall be tested separately for physical qualities, but for chemical analysis mixed samples may be used. Every sample should be tested for soundness, but the number of tests for other qualities will be left to the discretion of the engineer.

Chemical Analysis—18. The method to be followed for the analysis of cement shall be that proposed by the Committee on Uniformity in the Analysis of Materials for the Portland Cement Industry, reported in the Journal of the Society for Chemical Industry, volume 21, page 12, 1902, and published in Engineering News, volume 50, page 60, 1903, and in the Engineering Record, volume 48, page 49, 1903.

19. The insoluble residue shall be determined on a 1-gram sample, which is digested on the steam bath in hydrochloric acid of approximately 1.035 specific gravity until the cement is dissolved. The residue is filtered, washed with hot water, and the filter-paper contents digested on the steam bath in a 5 per cent solution of sodium carbonate. The residue is then filtered, washed with hot water, then with hot hydrochloric acid, approximately of 1.035 specific gravity, and finally with hot water, then ignited and weighed. The quantity so obtained is the insoluble residue.

Determination of Specific Gravity—20. The determination of specific gravity may be made with a standardized apparatus of Le Chatelier or other equally accurate form. Benzine (62° Baumé naphtha), or kerosene free from water, should be used in making the determination. The cement should be allowed to pass slowly into the liquid of the volumometer, taking care that the powder does not adhere to the sides of the graduated tube above the liquid and that the funnel

through which it is introduced does not touch the liquid. The temperature of the liquid in the flask should not vary more than 1° F during the operation. To this end the flask should be immersed in water. The results of repeated tests should agree with 0.01.

21. If the specific gravity of the cement as received is less than 3.10, a redetermination may be made as follows:

Seventy grams of the cement is placed in a nickel or platinum crucible about 2 in. in diameter and heated for 30 minutes at a temperature between 419° C and 630° C. After the cement has cooled to atmospheric temperature the specific gravity shall be determined in the same manner as described above. The cement should be heated in a muffle or other suitable furnace, the temperature of which is to be maintained above the melting point of zinc (419° C.) but below the melting point of antimony (630° C). This maximum temperature can be recognized as a very dull red which is just discernible in the dark.

Determination of Fineness—22. The No. 100 and No. 200 sieves shall conform to the standard sieve specifications of the Bureau of Standards, Department of Commerce and Labor.

23. The determination of fineness should be made on a 50-gram sample, which may be dried at a temperature of 100° C (212° F) prior to sifting. The coarsely screened sample should be weighed and placed on the No. 200 sieve, which, with the pan and cover attached should be held in one hand in a slightly inclined position and moved forward and backward in the plane of inclination, at the same time striking the side gently about 200 times per minute against the palm of the other hand on the upstroke. The operation is to be continued until not more than 0.05 gram will pass through in one minute. The residue should be weighed, then placed on the No. 100 sieve, and the operation repeated. The sieves should be thoroughly dry and clean. Determination of fineness may be made by washing the cement through the sieve or by a mechanical sifting device which has been previously standardized with the results obtained by hand sifting on equivalent samples. In case of the failure of the cement to pass the fineness requirements by the washing method or the mechanical device, it shall be tested by hand.

Mixing Cement Pastes and Mortars—24. The quantity of cement or cement and sand to be used in the paste or mortar should be expressed in grams and the quantity of water in cubic centimeters. The material should be weighed, placed upon a non-absorbent surface, thoroughly mixed dry if sand be used, and a crater formed in the center, into which the proper percentage of clean water should be poured; the material on the outer edge should be turned into the crater by the aid of a trowel. As soon as the water has been absorbed, the operation should be completed by vigorously mixing with the hands for one minute and a half. During the operation of mixing, the hands

should be protected by rubber gloves. The temperature of the room and the mixing water should be maintained as nearly as practicable at 21° C (70° F).

Determination of Normal Consistency—25. The normal consistency for neat paste to be used in making briquettes and pats should be determined by the ball method, as follows:

26. A quantity of cement paste should be mixed in the manner above described under Mixing Cement Pastes and Mortars, and quickly formed into a ball above 2 in. in diameter. The ball should then be dropped upon a hard, smooth, and flat surface from a height of 2 feet. The paste is of normal consistency when the ball does not crack and does not flatten more than one-half of its original diameter.

27. Trial pastes should be made with varying percentages of water until the correct consistency is obtained.

28. The percentage of water to be used in mixing mortars for sand briquettes is given by the formula:

$$y = \frac{P}{n + 1} + K$$

in which y is the percentage of water required for the sand mortar,

P is the percentage of water required for neat cement paste of normal consistency,

n is the number of parts of sand to one of cement by weight, and

K is a constant which for standard Ottawa sand has the value 6.5.

The percentage of water to be used for mortars containing 3 parts standard Ottawa sand, by weight, to 1 of cement is indicated in the following statement:

Percentage of water for neat cement paste.	Percentage of water for 1 to 3 mortars of standard Ottawa sand.
18.....	9.5
19.....	9.7
20.....	9.8
21.....	10.0
22.....	10.2
23.....	10.3
24.....	10.5
25.....	10.7
26.....	10.8
27.....	11.0
28.....	11.2
29.....	11.3

Determination of Soundness—29. Pats of neat cement paste of normal consistency about 3 in. in diameter, ½-in. in thickness at the center, and tapering to a thin edge, should be kept in moist air for a period of 24 hours. One pat should then be kept in air and a second in water, at the ordinary temperature of the laboratory not to vary greatly from 21° C (70° F), and both observed at intervals for at least 28 days. A third pat should be exposed to steam at atmospheric pressure above boiling water for 5 hours.

Determination of Time of Setting—30. The time of setting should be determined by the standardized Gillmore needles, as follows: A pat of neat cement paste about 3 in. in diameter and ½ in. in thickness with

flat top, mixed at normal consistency should be kept in moist air, at a temperature maintained as nearly as practicable at 21° C (70° F). The cement is considered to have acquired its initial set when the pat will bear, without appreciable indentation, a needle 1-12 in. in diameter loaded to weigh $\frac{1}{4}$ lb. The final set has been acquired when the pat will bear without appreciable indentation, a needle 1-24 in. in diameter, loaded to weigh 1 lb. In making the test the needle should be held in a vertical position and applied lightly to the surface of the pat. The pats made for the soundness test may be used to determine the time of setting.

Tensile Tests—31. Tensile tests should be made on an approved machine. The test pieces shall be briquettes of the form recommended by the Committee on Uniform Tests of Cement of the American Society of Civil Engineers, and illustrated in Circular 33 of the Bureau of Standards. The briquettes shall be made of paste or mortar of normal consistency. Immediately after mixing, the paste or mortar should be placed in the molds, pressed in firmly by the fingers and smoothed off with a trowel without mechanical ramming. The material should be heaped above the mold, and in smoothing off, the trowel should be drawn over the mold in such a manner as to exert a moderate pressure on the material. The molds should be turned over and the operation of heaping and smoothing off repeated. Not less than three briquettes should be made and tested for each sample for each period of test. The neat tests are not considered so important as the sand tests. The briquettes should be broken as soon as they are removed from the water. The load should be applied at the rate of 600 lbs. per minute.

Storage of Test Pieces—32. During the first 24 hours after molding the test pieces should be kept in air sufficiently moist to prevent them from drying. After 24 hours in moist air the test pieces should be immersed in water. The air and water should be maintained as nearly as practicable at 21° C (70° F).

Standard Sand—33. The sand to be used shall be natural sand from Ottawa, Ill., screened to pass a No. 20 sieve and retained on a No. 30 sieve.

34. Sand having passed the No. 20 sieve shall be considered standard when not more than 2 grams pass the No. 30 sieve after one minute continuous sifting of a 200-gram sample.

35. The No. 20 and No. 30 sieves shall conform to the standard sieve specifications of the Bureau of Standards, Department of Commerce and Labor.

The British Silk Exhibition will be held at Princess Skating Club Knightsbridge, London, S. W., under the auspices of the Silk Association of Great Britain and Ireland, June 5 to 19. The offices of the exhibition are at 3-4, Newgate St., London, E. C.

Turkish capitalists have asked their Government for a concession for the erection of a wire-nail works.

NOTES ON SEWAGE SLUDGE AND ITS DISPOSAL.*

By DR. Z. GROSSMAN.

From an economic point of view, the present mode of sewage disposal by water carriage is wasteful. In the course of sewage purification, the solids are separated by settling or precipitation processes at sewage works, to be further dealt with on the spot or elsewhere, whilst the liquid part ultimately finds its way into the streams and the sea. This part of the sewage, which contains valuable manurial constituents, is at present entirely wasted. If it could be advantageously used, it would represent a value of about £40,000,000 per annum in this country. This, however, is distributed over a quantity of 3,000,000,000 tons, and even if it were possible to recover the total amount of valuable constituents without any expense, each ton would only produce 3d. With a liquid of such complex nature as sewage, the recovery of its chemical constituents by chemical methods would be a hopeless task.

When the system of water carriage was adopted in this country, it was pointed out by Liebig that the system was economically wrong; but it was recognized that from a hygienic point of view it should be superior to any other system if properly carried out. So far as the liquid part of sewage is concerned, all anticipations can now be realized, but as regards the solid part of it, which has to be separately dealt with, the system has proved most disappointing from a hygienic point of view. A great point has been made of the fact that although those solids which constitute the sludge may not be all that can be desired from an aesthetic point of view, yet the pathogenic germs are but rarely found in it, and it has been argued that this proved that sewage sludge was not dangerous to health. This seems to me one of the fallacies which have crept into the consideration of the sludge disposal question. It is well known that the sampling of a substance for the purpose of analysis is even more important than the analysis itself. For chemical purposes, an average sample is sufficient; but in the case of a bacteriological examination of sludge, an average sample taken in the ordinary way is of no use. In a town of 100,000 inhabitants, in which one person is afflicted with a zymotic disease, the infection from that person will be contained probably in the accumulation of a couple of months' sludge, say in from 5,000 to 10,000 tons, and then only present in a very limited area, and in taking samples of the sludge, it is highly improbable that one would find pathogenic germs in the sample used for testing. In our present state of knowledge, it is impossible to separate a small bacterium bed from its surroundings. The fact that pathogenic germs have ever been found appears to me a proof that they must be far more prevalent than is at

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present accepted, and the same reasoning appears to me to apply to pathogenic germs which may find their way into the atmosphere from septic tanks, or from wet or dry sewage or sewage sludge.

In choosing a problem for research, especially one in connection with working up of by-products, the technical chemist has to consider the intrinsic value of the ingredients of the waste products, and whether their value as commercial products would be likely to leave a profit on the working expenses. When, however, it becomes a question of public health that a by-product should be rendered innocuous, expense should become a secondary consideration, and even if a method for the hygienic disposal of sewage sludge were to add to the expenses of sewage treatment, it would still leave a valuable asset in the improved health of the population.

The cheapest and simplest way of getting over the difficulty of sludge disposal is that of carrying the sludge, which may contain from 87 per cent to 92 per cent of water, out to sea in specially constructed boats and dumping it there. There appears to be always a danger that the tide may bring the sludge back to the nearest coasts; as is shown by the fact that it has occurred at Southend and other places on the estuary of the Thames, Llandudno, and other places; it has certainly been established that fish, including shellfish, may become contaminated and carry disease through coming in contact with sewage and sludge. In fact, it has become necessary to issue special government regulations controlling the working of oyster beds. This method of disposal can therefore not be recommended. The cost of dumping into the sea, calculated on the dry substance contained in the sludge, is given in the Royal Commission's Report as follows:

	Per cent dry substance.	Tons dry substance per annum.	Calculated on dry substance of sludge. per ton.
Glasgow	13.2%	40,000 tons at	40.9d
Salford	21 %	28,600 tons at	45.1d
Dublin	10 %	11,500 tons at	50.2d
London	8 %	200,000 tons at	56.9d
Manchester	14 %	23,600 tons at	68.9d
Southampton ...	10 %	1,395 tons at	169.0d

It thus appears that Salford, which is smaller than Manchester, is sending out more sludge, containing, moreover, 21 per cent of solids, a very large percentage; possibly Salford is not only disposing of the sludge it makes, but is also removing quantities of old sludge which in years past has been dumped on land and become concentrated through exposure to the air, but there is nothing in the Commissioners' Report to show whether such be the case. It is to be regretted that the report does not state the amount of sludge which may be obtained per 1,000 or per 100,000 inhabitants, and which at present is not known.

Probably in the majority of towns the process used consists in filter-pressing the settled sludge, and it is here where I found the greatest difficulties in ascertaining the actual cost of that process. If it is desired to dispose of the sludge by filter-pressing, it would be

necessary to know the costs of producing and disposing of a quantity of pressed cake equivalent to one ton of actual sludge. However, it is customary to state the results in quite a different manner, and in such a way as to render them useless for comparison. From my point of view, the quantity of water contained in a sludge cake is not the only thing to be considered, and going into the question on these lines we find discrepancies which have not appeared before, and which have in many cases led to the adoption of fallacious views. To give an instance of this, I may refer to the paper on "Sewage Sludge and its Disposal," read by Mr. A. B. Ogden in 1910 before the Association of Managers of Sewage Disposal Works. Starting with sludge containing 10 per cent of solid matter and 90 per cent of water, he states that in his work the average proportion of liquid sludge to one ton of cake is 2.73 to 1, and that the resulting cake contains 50 per cent of water. On the figures given, however, it appears impossible to obtain a cake of 50 per cent; the proportion of 2.73 to 1 corresponds to a cake containing 27.3 per cent of sludge, and even allowing 4 per cent for lime added before pressing, we can only account for 31.3 per cent of solid matter in the cake, which brings the percentage of water to 68.7, instead of 50 per cent.

To obtain such a cake, he calculates that it costs about 2s. per ton. This, in the 50 per cent cake which he assumes is obtained, would work out at 4s. and with a 31 per cent cake at 6s. 5d. per ton of dry matter, including the added lime. To compare the cost with other processes the calculations must be based on the 27.3 per cent of actual sludge, which corresponds to 7s. 4d. per ton of actual sludge. In this is not included the cost of the power used for filter-pressing, and instead of 4s. per ton on the dry material, it would therefore cost more than 7s. 4d. to remove one ton of actual sludge by filter-pressing, whereas the actual cost of removal by steamer is stated to be 5s. 9d. per ton.

The above instance is not an isolated one, and should prove how important it is to reduce the calculations to dry sludge as a basis. Pressed sludge cake nearly always contains lime and, in many cases, other ingredients which have been added in the settling tanks, and which by increasing the bulk of the solid matters and apparently decreasing the amount of water are liable to lead to erroneous conclusions. The Royal Commissioners have also overlooked the importance of reducing facts to a common basis. The costs for pressing given in their report vary from 1s. 11d. to 6s. 4d. per ton of sludge cake in different localities; some of the sludge has been obtained from sedimentation tanks without the addition of chemicals, some with the addition of chemicals, some from septic tanks; the proportion of lime added for pressing varies from 1.3 per cent on the sludge to 20 per cent. In no case is the amount of water in the original sludge or the amount of water and added chemicals and lime in the finished pressed cake given. The primary object for which filter-pressing was introduced seems to have

been lost sight of. That object was to lessen the cost of removal by reducing the bulk and weight of sludge which would be obtained from the settling tanks, and which on an average contained nine tons of water to every ton of dry substance. It is, however, quite feasible to obtain a sludge containing four tons of water to every ton of dry substance by settling and draining, and if a sludge cake after addition of chemicals does not show a very decided increase over 20 per cent in the percentage of actual sludge, there appears to be no advantage in going to the expenses involved in the processes connected with filter-pressing. The same principle will apply in the examination of other processes which aim at the reduction of the bulk of the original settled sludge. In one of these, the water is separated from the solids by centrifuging in a highly ingenious machine constructed by Schafer ter Meer. A report of the results obtained is to be found in the "Communications from the Royal Testing Institution of Berlin for the Supply of Water and for the Removal of Sewage and Waste Liquors in Berlin." At the request of that institution one of the building inspectors, Mr. Reichle, and Professor Dr. Thiesing, carried on a series of experiments, in which the cost of filter-pressing is given as 2s. 4d. per ton and that of centrifuging 3s. 5d. per ton, but as they do not state the amount of water in finished products nor the amount of foreign substances added (in the case of filter-pressing it appears that fine coal was added) it is impossible to determine the relative costs of the two processes calculated on the dry sludge. It appears clear that after centrifuging the mass only contains from 26 per cent to 30 per cent of dry substance. Assuming that the pressed cake containing the same amount of actual sludge, say 28 per cent, then the relative costs, calculated on dry sludge, would come to 8s. 4d. by filter-pressing, and 12s. 2d. by centrifuging. Apart from the increased expense, a drawback to the centrifugal method is that only about 60 per cent of the sludge passing through the machine is effectively dealt with, and the rest has to be settled again, and to be passed through the machine a second time, and so on. It has been contended that the sludge leaving the centrifugal machine can be stored for any length of time without causing a nuisance, or put on the land without further manipulation, but I am informed that in Frankfort, where several of these machines are working, it has been found necessary to put down a drying machine, which will add still more to the expense of centrifuging. In any case, the local circumstances in this country are such as would render it unlikely that his centrifugal machine would be generally adopted.

In the course of these investigations, it occurred to me to calculate what would be the cost of producing the same result as in a filter-press or centrifugal machine by means of heat. There is no difficulty in obtaining a sludge of 20 per cent solid actual sludge and 80 per cent of water by settling. Taking the sludge obtained by centrifuging or filter-pressing to contain

33 $\frac{1}{3}$ per cent of solids and 66 $\frac{2}{3}$ per cent of water, I calculated how much water would have to be removed from the 20 per cent settled sludge in order to convert it into a sludge with 33 $\frac{1}{3}$ per cent of solids and 66 $\frac{2}{3}$ per cent of water. In order to obtain three tons of 33 $\frac{1}{3}$ per cent sludge one would have to evaporate two tons of water from every five tons of the 20 per cent sludge. I had previously found that in a drying machine for sludge, which I constructed for the purpose and a description of which is to be found in Eng. Patent No. 26,516 of 1909, I could evaporate nearly six pounds of water per pound of low grade coke or coke breeze, and as the price of this material varies from 5s. to 7s. 6d. per ton, a reduction in bulk of sewage sludge which had been previously settled down to 20 per cent to the consistency of the cake obtained by filter-pressing can be obtained at a cost in fuel of from 1s. 8d. to 2s. 6d. per ton, calculated on the dry material; to obtain the same result by filter-pressing or centrifuging costs more than from 8s. 4d. and 12s. 2d. per ton, so that so far as the reduction in bulk goes, the method of evaporating by heat is cheaper than any other. Of course, other expenses have to be added to this for labor, capital charges, etc., but even then, the partial desiccation by heat is cheaper than filter-pressing or centrifuging in Schafer ter Meer's machine.

The disposal of sludge by shallow burial in the ground can only be resorted to in cases where large tracts of land are available close to the sewage works, and even then there is a residue left which, sooner or later, may have to be dealt with if the land is not to remain worthless, and also there is a possible danger to health from pathogenic germs.

As regards lagooning, the same considerations apply, and there is probably no case in which lagooning does not produce a nuisance and possible danger to the neighborhood. I will, therefore, for the present, confine myself to the processes which are most in vogue for the further manipulation of the sewage sludge after it has been pressed. The course generally adopted is that of dumping the pressed sludge on land which has been bought for the purpose. But in many towns land suitable for that purpose is nearly filled up, and it is becoming a serious question what will have to be done when there is no more land available for dumping. In some cases, farmers will cart the stuff away for nothing; in some they will even pay a small sum for it, but even there it will only be removed during winter and spring, and left at the sewage works in summer, when it is most desirable that it should be shifted. Experiments on the value of sludge as a manure have been made at the instigation of the Royal Commissioners, and published in a special report, in which it is distinctly stated that no sludge is worth 10s. per ton on the dry matter in it. This shows that sewage sludge can never become a marketable article which will pay the producer. Small works situated in the center of a large farming district may be able to dispose of their sludge to farmers who may find that the sparing use of sludge on their land

pays for the cost of cartage, but in the majority of cases, it would be necessary to distribute the sludge at a considerable distance from the works, and in that case, the cost of cartage, commission to salesmen, and other items would, on an average, far exceed the value of the sludge. The evidence given by sewage engineers before the Royal Commission shows that they recognize the fact that sludge is worthless as a commercial product for agricultural purposes, and the general opinion appears to be that practically the only constituent in the sludge which is valuable to farmers is the lime which is added to the sludge before pressing, and which often amounts to a considerable percentage of the sludge.

In Appendix VIII, which treats with the manurial value of sewage sludge, these points are clearly set out, and one would have expected that the commissioners would endeavor to find some reason why the results obtained with sewage sludge on land should be out of proportion to the amounts of nitrogen, potash, and phosphates which it contains, but I cannot find that they have done so, and what appears to be the most natural reason for it has been overlooked altogether. It is well known that every sludge contains fatty matter, arising from soapsuds, and other domestic refuse. Notwithstanding this, the amount of grease contained in the sludges used for the experiments on land was not determined. Had this been done, it would have been found that it is the grease which interferes with the action of the manurial constituents of the sludge. Fatty substances mixed with mineral and organic matter will produce a kind of magma impervious to rain and air, and the deleterious effect of the presence of grease in manures has been recognized before. In the article on artificial manures, in "Thorpe's Dictionary of Applied Chemistry," Warrington says, on p. 504, vol. 2, 1891 edition, with regard to fish manure. "The practical value of the manure depends to some extent on the quantity of oil present; the smaller the quantity of oil the more readily does the manure decompose in the soil." Now fish manure contains more than five times the amount of phosphates, which sewage sludge contains, so that if its proportion of grease were to render inoperative such an amount of nitrogen and phosphates as is contained in sewage sludge, there would still be a large amount of these constituents available to act on the plants, and though of less value than a similar manure which contained no grease, fish manure would still produce good results; in sewage sludge, however, the grease predominates to such an extent as to render the manurial constituents practically inoperative.

In the experiments carried out by the Royal Commission, it was found that nothing was gained by drying sludge before applying it on land; in fact, it is stated that dried sludge produces worse results than wet sludge. Mr. Ogden, however, in the paper referred to above, evidently does not accept these facts and values the dried sludge manufactured at the Manchester Sewage Works at £1 per ton, or double the

amount which has been found to be its utmost value by the Royal Commission. The cake which is obtained from the filter-presses is compressed into blocks 9 in. cube, and these blocks are dried on iron plates heated from waste steam from the engine. Even if it were possible to establish a market value of 20s. for the dried sludge, which, in the face of the Royal Commission's Report, is not probable, it would not pay to produce dry sludge in the manner which he has apoted. There is comparatively little steam required in a sewage works for the purposes of power, and the quantity of sludge which could be dried with waste steam would only be a small fraction of the total production. Sludge is a bad conductor of heat, and in his mode of drying, which is one of the least economical, it would be impossible to get the heat to penetrate into the center of the cubes, so that neither a sufficiently dried cake would be obtained nor would any germs contained in the sludge be sterilized. If the coal had to be paid for in the drying it would add at least 3s. 6d. per ton for fuel, and the several items which he enumerates will stand as follows:

	S.	d.
Pressing	6	5
Cutting cakes, etc.....	3	6
Drying	3	6
Bags	4	0
Total	17	5

The total cost would come to 17s. 5d., leaving 2s. 7d. to pay for carriage, cartage, commission to salesmen, and general charges and bad debts. Thus there is the certainty of a substantial loss on each ton of dry sludge sold. Mr. Ogden mentions in his paper that the dried sludge which he obtains is pyrophoric and thus liable to spontaneous combustion, and for that reason it is ground shortly before dispatch; that fact may lead to difficulties with the insurance and railway companies.

It appears from Mr. Ogden's paper, and from the annual report for the year ending March 29, 1911, of the Rivers Department of the City of Manchester, that experiments have been made with the Manchester pressed sludge cake with a view to gasifying it in a generator. Four tons of sludge cake containing 50 per cent of water were mixed with one ton of coal and gasified in a producer, and the report which Messrs. Crossley Bros. have given (Rivers Department Report, p. 20) is as follows:

"We are pleased to inform you that we have succeeded in gasifying this material up to a moisture content of 50 per cent to 55 per cent. Our yield shows 80,000 cubic feet of gas of a calorific value of 112 B. T. U.'s net at N. T. P. and the equivalent of 61 lbs. of ammonium sulphate per dried ton gasified, when dealing with material of nitrogen content 1.46 per cent. Our only difficulty consisted in thoroughly cleaning the fire with such a material containing 40 per cent of ash, for dealing with which our small experimental plant is indifferently equipped."

Practically the same figures are given in Mr. Ogden's paper with the following further particulars:

One ton of coal equals 160,000 cubic feet of gas, 28½ tons of gasified coal equals one ton sulphate of ammonia. Calorific value 154.6 B. T. U.'s per cubic foot, combustible gas 40.3 per cent.

On the strength of these data, the following comments are made in the annual report of the Manchester Rivers Department (p. 20): "With specially designed plant and a larger proportion of coal, the above results indicate that where use exists for power, the pressing of the sludge with small coal and subsequent gasification may afford a satisfactory means of its disposal."

I have calculated the actual facts from the figures given, and I find that the actual amount of gas due to the sludge comes to 26,000 cubic feet of a calorific value to 28.5 B. T. U.'s, and the sulphate of ammonia per dried ton of sludge would only amount to a little over 20 lbs., which is less than that of coal by the ordinary process of dry distillation, and one-fourth that which would be obtained in the production of Mond gas from coal.

The calorific value of the gas obtained being absurdly low shows that more than five tons of sludge cake would be required to give the equivalent of the available thermal value produced by one ton of coal, and including the removal of the clinkers more than six tons of material would have to be handled to obtain the same results as could be obtained from one ton of coal. The generator part of the plant also would have to be proportionately larger and more expensive. Reducing the whole to money values it means this: that one would have to pay probably five times the amount that an ordinary gas producing plant would cost, and that one would have to pay about £2 for fuel in the shape of sludge against 8s. 6d. per ton for which coal can be bought at the Manchester Sewage Works. There is nothing said about the commercial side of this question in Messrs. Crossley's Report, which quite properly only states that there appears to be a likelihood that the purely engineering difficulties of the problem might be overcome, and I fail to see what useful purpose can be served by stating, as is one in the Manchester Report, that this method may yield satisfactory results. A calculation based on the thermal value of sludge would have shown that it is hopeless to gain a satisfactory yield in power or heat from sludge cake with 50 per cent water in a generator, and the results obtained by Messrs. Crossley Bros. fully confirm this.

Quite recently the plan of gasifying sludge in gas retorts, which I advocated more than thirteen years ago in a paper read before the society, has been resuscitated in Germany. I stated then that if the engineering difficulties could be overcome, there was a prospect of that method being practicable. I have since come to the conclusion that though from a purely technical point of view my statement was correct, it would be out of the question that a process of that kind could be worked in this country, in which the gas works are in nearly every case owned by corpora-

tions, and in which the profit from the gas works helps to relieve the rates. The plant for the dry distillation of sewage sludge would be far more expensive than that used in the case of coal. The quality and quantity of the gas would entail additional expense and inconvenience, as sewage works are generally at a considerable distance from the towns. Again, it might cost nearly £2 to obtain a quantity of sludge equivalent to one ton of coal. I have finally, after serious thought, abandoned the idea on which I first started in connection with the disposal of sewage sludge, and devoted my endeavors to my process of distillation with superheated steam, and which, I have found, has none of the objections either from an economic, engineering, commercial, or hygienic point of view, which the other method has.

The hygienic disposal of sewage sludge is the key-stone of sewage purification, and the most rational mode of sludge disposal is that of putting it back on the land. But to use it in the shape of sludge, wet, pressed or dried, for farming purposes is, nearly always impracticable and always open to serious objections on hygienic grounds. There will always be a suspicion that it may disseminate disease amongst cattle and human beings; it should never be used where cattle is grazing, and not where the plant shoots have appeared above ground; its use in the latter case is, I understand, forbidden by law in France. Ordinary drying of sludge is no guarantee of sterilization. To make the sludge available for farming purposes it must be deprived of its grease, and the residue exposed to such a temperature as will be a guarantee that it is thoroughly sterilized. It is these considerations which I have borne in mind in working out my process for the disposal of sludge by means of distillation with superheated steam in such manner as will comply with the severest requirements of hygiene.

DISCUSSION.

Mr. W. Thomson said that the cost of the author's process of drying sludge could be very easily verified. According to Dr. Grossmann, the cost of coal for direct drying by heat would be from 1s. 8d. to 2s. 6d., as compared with 8s. 4d. to 12s. 2d. by filtration, and 5s. 9d. for removing it in the wet condition by boat which was the present practice in Manchester and Salford. That involved the hygienic question that in such deposits there was a chance of inoculating the fish and rendering seaside resorts objectionable. The disposal of large quantities of refuse solid material near large towns constituted a most difficult problem, as the available land soon got filled up. Besides drying the sludge, Dr. Grossmann's process recovered most of the grease which was a valuable product, and left a dry, sterilized material which possessed manurial value much greater than the wet, greasy and slimy stuff produced from the partially dried sludge. Both from its physical constitution and from some of its constituent parts, it seemed to constitute a valuable manure. One of the medical officers of health spoke to him most enthusiastically of its value as a manure from the re-

sults obtained by him from comparative experiments made in flower pots and on the soil in his own garden.

Mr. R. H. Clayton inquired with respect to the figure of 40,000,000 pounds what percentage was solid and what liquid. It seems a great pity that all the constituents were lost. In a book dealing with the natural resources of America, it was stated the crust of the earth only contained 0.1 per cent of phosphorus, and there was no chemical method known at the present time of manufacturing phosphates. Phosphorus had a very great bearing upon agriculture. In Wisconsin, farming the land according to the American method, they had reduced the phosphoric acid contents from 2,800 lbs. per acre down to 1,800 lbs. in the 8 inches of virgin soil. That difference had to be replaced by fertilizers. As a consequence of the American methods of farming, the "corn belt" had gone right back nearly to the West.

Mr. S. S. Platt agreed with much that Dr. Grossmann had said, but until they had had the process outlined in his previous paper worked out on a sufficiently large scale so that they could really determine what the cost was and what were the commercial benefits, he did not think they could make much progress. It was all a question of expense. The process was to be worked on a large scale at Oldham where there was no grease beyond what came from the slopstones. If the process proved satisfactory there, then the result should augur well for those towns which had a considerably larger quantity of grease in their sewage than Oldham.

Mr. G. Gunn believed the system of multiple evaporation could be tried very cheaply. The Yorkshire woolcombers had had a system of recovering grease, in which they also recovered the free ammonia in the distilled water from the evaporator which was returned to the works for washing purposes. That might not be a commercial proposition at present, but he thought it was worth considering.

Mr. W. H. Coleman observed that in France there were several large installations where the separation of the domestic portion of the sewage was undertaken, and where ammonia was recovered in fairly large quantities. The two chief towns were Angers and Bordeaux.

The chairman mainly agreed with Dr. Grossmann's statements, but differed in one or two matters of fact.

The question of pathogenic germs was one upon which very little was known. It would be a very good thing if they could adopt some better method of dealing with sludge than dumping it down among the fish. He had seen centrifuges in Frankfort, and his impression was precisely that of Dr. Grossmann. They did not reduce the moisture to a very great extent, and there was a very considerable proportion of unpurified liquid. In his opinion, the one advantage was that the sludge was delivered in a granular condition, so that it could be readily passed along a traveling band into a dryer, and, being loose, dried more readily than pressed cake. At Ostend they had sludge presses at

work side by side with centrifuge presses which rather indicated that the sludge press was the simpler. He was afraid a good deal of Dr. Grossmann's argument was built up on a wrong figure, because he took 33 per cent as being the solid content of pressed sludge. Though he (the speaker) would not pin himself to more than 50 per cent, as being a round figure, it was certainly more than 33 per cent, one might certainly say 45 per cent with Manchester pressed cake, which was the only one he could speak of, as an average. Sludge calculations were extremely difficult to follow, and he quite agreed they ought to thank Dr. Grossmann for the hint. In reference to the relative solids between Manchester and Salford, it was quite true that for many years Salford dumped its sludge into an old dry sludge pit, which raised the solid content considerably; but in making comparisons it was necessary to have the facts right. Lagooning was not altogether satisfactory, but he did not agree that digging into the soil would necessarily come to an end, for the simple reason that the sludge, after a period of shallow burial, not of deep burial, was completely disintegrated, and the land was actually benefited and loosened thereby. He was entirely in agreement with Dr. Grossmann with regard to the question of grease, and had always wondered why the Royal Commission should have overlooked the matter. Perhaps Dr. Grossmann had not sufficiently considered the point of Mr. Ogden's paper, and it was to be regretted that that gentleman was not present to answer the criticism that the sludge dealt with by him did not contain any great, and was not sewage sludge properly speaking, but was humus material washed out of the filter beds. They would readily admit that to dry the whole of the Manchester sewage sludge with the waste steam available at the sewage works was a very big proposition. With regard to the matter of power production, the point was simply that many sewage works had destructors attached to them, by means of which the sludge was finally and hygienically got rid of, though at a price.

Dr. Grossmann, in reply, said he had had to go somewhat against the ordinary groove in which things were accepted in sewage works. He had calculated the relative values of solid and liquid matter in sewage in different ways, but it was extremely difficult to determine them. In the middle of the last century Liebig was asked by the London Metropolitan Authority to present a report on the water carriage system, and in consequence made a series of calculations in which he apparently made allowances for everything, and the proportion between solid and liquid appeared to be as between 1 to 20 and 1 to 40; to get nearer to the relative values in the present condition of things was not possible. He hoped to be able to convince Mr. Platt that the process which had been adopted in Oldham was not only effective, but also satisfactory as regards cost. He felt, from the tone of the discussion, he had done right in bringing the matter forward, and that the points he had raised required clearing up.

The evaporation of the liquid part of sewage was a very large order, and he did not see how it could be done. Mr. Coleman mentioned it was done in France, and, though that was correct, still it was not done under the water carriage system, in which about 30 gallons of water per person was added and would have to be evaporated. In the places in France referred to by Mr. Coleman, the sewage was not mixed with water. In Manchester, before the general adoption of the water carriage system, as much as 10,000 tons of manure was made from middens by evaporation; that had a high reputation among farmers; but the old system had been condemned on hygienic grounds, and there was no doubt it was now dead. They were committed to the water carriage system, which was, in his opinion, from a hygienic point of view, by far the best system, and they stood to get back in health what they lost in money. He was of opinion that even if it were only doubtful whether a product might carry infection, the best plan to adopt where it was a question of public health would be to do away with it altogether. He was also pleased that Dr. Fowler agreed with his remarks on Shafer ter Meer's centrifugal machine. He could not agree with Dr. Fowler upon the question of percentage of sludge in pressed cake. The average percentage of total solid matter in cake was under 40 per cent; this contained on an average from 4 to 6 per cent of lime which had been added to it. There was an impression that but little lime was in the cake, as its quantity was calculated on the original sludge. It sounded very little to add one per cent of lime to sludge, but that sludge contained only 5 or 10 per cent of solid matter, and thus on the dry material the lime amounted to 10 or 20 per cent in the end; not many cakes, therefore, contained more than 33 per cent of sludge. It was not quite clear from Dr. Fowler's remarks whether he had read Mr. Ogden's paper, which stated distinctly that that gentleman worked with sewage sludge from the settling tanks, of which he used 2.73 parts at 10 per cent solids to obtain one part of pressed cake. It was evident on these figures, that the Manchester pressed cake as produced by Mr. Ogden could not possibly have had more than 27.3 per cent of actual sludge in his pressed cake; all the statements made by him (Dr. Grossmann) could be verified by reference to that paper; his arguments were not built on wrong figures or assumptions. With regard to Dr. Fowler's remarks on gasifying and dry distillation it must be borne in mind that the calorific value of the sludge was low, and in any scheme of gasifying in producers or of producing illuminating gas by dry distillation one would have to reckon with the fact that one had to compete with coal at from 7s to 15s per ton, whilst a quantity of sludge capable of producing the same results would cost nearly 40s and require much larger plant, and handling of five or six times the weight of an equivalent quantity of coal, and he could therefore not agree with Dr. Fowler's views on the practicability of these methods.

WHAT MAKES WHITE LEAD CHALK AND HOW CHALKING MAY BE PREVENTED.*

By HENRY A. GARDNER†.

Chalking and Repainting.—The chalking of white lead is one of the evils attending the use of this valuable white paint pigment which the master painter is most anxious to correct. Every fair observer will probably admit that moderate chalking is not objectionable, as it leaves a surface for repainting which will quickly receive and amalgamate with the new paint applied; this result being difficult with an old painted surface which is excessively hard or brittle. Excessive chalking, however, which is often followed by deep alligating and gradual disintegration, should be avoided if possible, for no matter how good a paint may be placed over a deeply-checked surface, the result is always unsatisfactory and unsightly.

The writer has recently read with interest a pamphlet which attempts to explain the cause of the chalking that is exhibited by nearly all pure white lead paints after exposure to the elements. In the article referred to, some very interesting theories have been advanced, and the object of this paper is to briefly outline these theories and discuss them in the light of the most recent knowledge obtainable on the subject.

Oil Conservation or Oil Substitution.—It has been stated in the pamphlet referred to that the chalking of white lead is due to the lack of linseed oil, and that chalking would not take place to any extent if white lead paints were mixed with greater quantities of linseed oil. From an economical standpoint it would appear to the writer that if painters were to follow the above suggestion and use greater quantities of linseed oil than is at present the prevailing practice the effect would not be towards relief from the present high prices which must be paid for pure oil, and might not only encourage the use of linseed oil substitutes which have not been thoroughly tested, but actually lead to the use of such substitutes.

Short Oil and Long Oil Reductions.—It has further been stated that not only the priming coat of white lead but the top coat as well should receive very long oil reductions in order to form a film which would protect the pigment from the elements, which are the initial cause of chalking when lead is applied with the usual short oil reduction. The application of ordinary white lead paint has been compared with the application of short oil varnishes which contain quantities of gum with very little oil, the analogy suggesting that the same enduring results which are obtained on exposure of long oil varnishes would be obtained if lead paints were reduced with quantities of oil. Commenting on the above procedure, it would appear to the writer that the use of larger quantities

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of oil than are at present in common use would result in a paint deficient in hiding power and strength. Furthermore, the comparison of varnishes with paints is not justified, as a varnish which consists of gums dissolved in oil is an entirely different material from an oil in which pigments are simply suspended. Both of these materials must be studied along separate lines, as they are physically and chemically different.

Amount of Oil Determined by Pigment.—It is well known that linseed oil, or, in fact, any oil, when spread into a paint films to a coating which upon exposure does not possess any very great strength or moisture-excluding power. When linseed oil, however, has been ground with pigments, the strength of the films is increased materially, and the greatest strength is developed in those cases in which a critical percentage of pigment has been added to the oil. The critical percentage varies with the nature of the pigment, a small quantity of some pigments being sufficient, while a large quantity of other pigments is necessary, to produce films of maximum strength. An average paint consists of 10 lbs. of pigment suspended in 1 gal. of oil, but the writer has in mind at present a paint made from 35 lbs. of pigment suspended in 1 gal. of oil. This pigment, namely American vermilion (basic chromate of lead), is probably the lowest oil-carrying pigment ever produced or applied under actual practical conditions, and today, after nearly four years' exposure along the Atlantic coast, where it has been subjected to the most severe atmospheric conditions, it is in almost perfect condition, showing absolutely no chalking. Being a lead pigment and being applied with a shorter oil reduction than white lead has ever been applied with the result would seem to dispose of the theory advanced that white lead should be applied with longer oil reductions. If the amount of oil and not the amount of pigment should determine the service of the paint, would not a pigment such as asbestine, which requires enormous quantities of oil, form a paint more durable than white lead or any of the other white base pigments? We all know, however, that this is not wholly the case, and moreover, we must look at the question in a practical manner, for the hiding power of a paint is one of the most important properties.

Hydrate and Carbonate.—The percentage of lead carbonate in corroded white lead determines its hiding power, while the percentage of hydrate determines the oil carrying capacity. When the amount of carbonate runs to 80 per cent the lead has a high gravity and takes only $3\frac{1}{2}$ gals. of oil to 100 lbs. of paste lead to produce an easy-spreading paint that will have good hiding properties. When the amount of carbonate in corroded white lead drops to 60 per cent and the hydrate reaches 40 per cent difficulty in grinding is observed, even if additional oil is added. Such a product is likely to harden and becomes gummy in the package, and upon thinning one hundred pounds of paste for application six gallons of oil

are required and the product has only slight hiding power. Corroded white lead that contains about 70 per cent lead carbonate and 30 per cent lead hydrate is probably the best grade that can be obtained; its oil absorption is medium and its working properties and hiding power excellent.

Amalgamation.—The claim has been advanced that the application of long oil leads in repainting work is desirable, on account of the penetration into the old paint that can be secured from the newly-applied paint, both amalgamating to form one solid film. If this phenomenon really took place under such conditions, a cross section of the film produced would probably appear under the microscope as one solid mass of pigment of oil. As a matter of fact, this is not the case, as an examination of photomicrographs will show.

The Effect of Tints on Durability.—It is very generally admitted that tinted paints are far more durable than white paints. In the article under discussion, the claim is made that the increased durability of tinted paints is due entirely to an increase of oil brought to the white paint by the coloring pigments, all of which have rather high oil carrying properties. As a matter of fact, however, the amount of oil carried into a white paint by one or two per cent of tinting color is too small for consideration and is quite insufficient to give the result claimed above. White leads made by various processes take up varying amounts of oil, 100 lbs. of some paste leads requiring only $3\frac{1}{2}$ gal. of oil, while in other cases leads made by different processes require as high as 6 gal. of oil to produce paints of a relative consistency. Upon exposure of such leads there seems to be no material difference in the way they wear. This results would further indicate the fallacy of claiming that the extra durability obtained from tinted paints is due to the slight increase of oil brought to them as a contribution from the coloring matter used. We must attribute the greater durability of tinted paints, therefore, to the nature of the added tinting pigments and to the differing physical and chemical properties which they bring to the white base.

Carbonate and Oxide Pigments.—The carbonate pigments, such as lead carbonate, calcium carbonate and barium carbonate, would all chalk when painted out and exposed to the elements. This chalking seems to be a distinct feature of the carbonate pigments. While it is true that certain other pigments which are not carbonates chalk quite heavily, it is further more true that the exception proves the rule. Pigments which are not carbonates, but which have other radicals, and which will probably be more readily recognized if called by their trade names, such as red lead, zinc white, litharge, etc., do not possess chalking tendencies, and they form paints which remain hard and glossy under long exposure. When either carbonate pigments or oxide pigments are reduced with short or long oil reductions, the same conditions hold true. It would become at once apparent, therefore, that if

the chalking tendencies of the carbonate pigments are to be overcome and corrected, or the excessive hardness of the oxide pigments is to be reduced, a mixture of the two in correct proportions should solve the problem. As a matter of fact, mixtures of this type do not become excessively hard, nor do they chalk to any great extent, and, although this principle was long ago discovered, and has been used for years by progressive painters, it must be stated over and over again in order to convince those who are not thoroughly familiar with the results of paint tests.

Conclusions.—After considering the present practice of some of the leading members of the association, and summing up the results obtained from practical tests made throughout the country, the writer has formed the conclusion that the paint best suited to withstand service is a tinted paint made of a proper mixture of pigments, carefully ground together and applied by a painter, for even the best paint made must be applied by skillful hands, backed by intelligence, if the best results are to be obtained.

According to a joint press bulletin given out by the U. S. Geological Survey and Bureau of Soils, a potash deposit of apparently great importance has been discovered at Borax or Searles Lake in the north-western corner of San Bernardino county, California. This lake or playas is the last remaining pocket of a once much greater lake which has almost dried up and its central depression contains a large body of crystalline salts known to consist of common salt and sulphate and carbonate of soda with smaller quantities of borax. This salt body is saturated with brine, and interested persons stimulated by the governmental search for potash recently secured an analysis of old sample material from this brine. The result being significant, the lake was visited jointly by representatives of the Geological Survey and of the Bureau of Soils who took brine samples from six wells distributed over the salt flat. Analyses of these samples have been made by the co-operative laboratory at the Mackay School of Mines, at Reno, Nevada, and show an average of 6.78 per cent of potassium oxide (K_2O) in solution. The average salinity of the brine is 43.82 grams of solids per one hundred cubic centimeters. Comparison of the results indicates that the brines are nearly uniform throughout the flat. The probable importance of the deposit is due to the occurrence of the potassium salts in soluble form in a natural saturated brine, and under climatic and other conditions especially favorable to its separation and recovery by solar evaporation. Existing data give reasonable assurance that the brine saturated salt body is at least 60 feet thick and covers an area of at least eleven square miles. Assuming the salt body to contain 25 per cent by volume of the brine, the total amount of potassium oxide is estimated at over 4,000,000 short tons.

THE "LUMINATOR" TREATMENT OF WATER.*

By HENRY B. LAKE.

There appeared in Volume XXX. (1910), page 933, of this Journal†, an abstract of a paper read before the New York Section, entitled "A new treatment of water by means of aluminum plates, for preventing scale in boilers without the use of chemicals." Therein it is held that hard water when allowed to flow over aluminum is ionically changed, so that on boiling scale is not formed, the temporary hardness is reduced, and the water so treated acts as a detergent on existing scale, converts the red oxide on boiler plates to black oxide and maintains the plates black, while the scale-forming salts are precipitated as sludge instead of adhering as scale. It is stated, on the contrary, that where water is being treated continuously day and night it is necessary to give the apparatus a weekly rest; that the best results are obtained when the "luminator" is disposed north and south and exposed to direct light, also that "in the dark the apparatus almost ceases to work."

With the object of discovering what is the effect of passing water over aluminum the following experiments were undertaken:

Experiment No. I.—A large sample of water was taken from the city service tap in the laboratory. A strip of aluminum 2 in. wide by 10 ft. long by about 12 gauge in thickness was formed into a channel V-shaped in section, and was disposed due north and south, and dipping to the north at an angle of 15° . Part of the sample of water was filled into a "Winchester" bottle provided with a syphon tube, the outlet being controlled by a screw pinch clip. This bottle of water was supported at the head of the aluminum chute, and a graduated measuring cylinder was placed at the lower end of the chute. The chute was facing north, daylight. Water was then allowed to flow down the chute, and the rate adjusted until the speed was 1 litre in 17 minutes. After discarding several lots, 500 c.c. were collected.

Experiment No. II.—A further quantity of water from the same samples as used in Experiment No. I. was passed in exactly the same manner, but the aluminum chute was replaced by an aluminum tube, also 10 ft. long by $\frac{1}{2}$ -in. internal diameter. Velocity of flow of water and position of tube were identical with the chute treatment.

To ascertain the effect produced on the water, the original, and the water treated as in Experiments I. and II. (Table I.) were submitted simultaneously to the following tests: Total hardness by soap solution; permanent hardness by soap solution; mineral analysis.

Before giving the tabulated results, a brief description of the method employed for the mineral analysis should be given:

*From the Journal of the Society of Chemical Industry.
†Journal Society of Chemical Industry.

The water in each case was evaporated to dryness and the residue treated with hot distilled water and filtered, thus separating the insoluble carbonates from the more soluble sulphates. This separation is not absolute, but is largely effective, and it has been proved by constant use on all kinds of waters to effect a general separation; and when certain precautions are taken, repeat separations can be made with corresponding results. The water-soluble portion was set aside, and when cold was also made up to the original volume with distilled water. The insoluble portion was dissolved with the aid of a few drops of hydrochloric acid and hot water, and when cold was also made up to the original volume. Both portions were then submitted to estimations of calcium and magnesium. The calcium and magnesium in the soluble portion were combined with sulphuric anhydride, separately determined, and the calcium and magnesium in the insoluble portion were combined with carbonic anhydride separately determined in the original sample of each lot of water.

The results tabulated are shown in Table I.

aluminum chute and tube, and thus discover a difference between water so "alumed" and "luminated" and some of the same water only "alumed." Also, in order to show only the difference in permanent or residual hardness after boiling, all the samples were subsequently boiled and the precipitate filtered off.

The aluminum sulphate added to each sample was in the form of a clear solution of known strength, and it was added to each water in quantity equivalent to 3 parts of alumina per 100,000. The velocity of flow for the samples passed over metallic aluminum was 1 litre in 6 minutes. The resulting solutions then afforded the following results:

Experiment V.	Mineral analysis. Ionic determinations parts per 100,000.				
	Hardness by soap.		Insoluble.		Soluble.
	Permanent		Cal- cium.	Mag- nesium.	Cal- cium.
					Mag- nesium.
+ Alum.					
Original water.....	40.0°		0.47	0.23	3.18
After passing chute....	36.2°		0.63	0.20	2.70
After passing tube....	37.8°		0.59	0.23	3.00
					4.58
					4.58
					4.46

The effect of the treatment with aluminum sulphate is very evident if this table be compared with the re-

TABLE I.

Experiments I. and II.	Mineral analysis, parts per 100,000.									
	Hardness by soap solution (French scale).		Ionic estimations.				Combinations on evaporation.			
	Total. Permanent.		Insoluble.		Soluble.		Insoluble.		Soluble.	
			Cal- cium.	Mag- nesium.	Cal- cium.	Mag- nesium.	Calc. carb.	Magnes. carb.	Calc. sulph.	Magnes. sulph.
			Velocity of flow, 1 litre in 17 minutes.							
Original water.....	70.5°	39.6°	9.12	1.58	0.42	4.53	22.80	5.46	1.52	22.38
After passing (1) aluminum chute.....	70.5°	38.8°	9.42	1.74	0.35	4.47	23.55	6.02	1.19	22.08
After passing (2) aluminum tube.....	70.0°	38.2°	9.07	1.59	0.35	4.59	22.69	5.50	1.19	22.67

Experiments I. and II. as fully described were then repeated, the only difference being that the velocity was increased from 1 litre in 17 minutes to 1 litre in 6 minutes by increasing the angle of inclination of the chute and tube from 15° to 70° to the horizontal. Determinations of the total and permanent hardness only were made on these samples, as follows:

Experiment III.	Hardness (French scale) by soap solution.	
	Total.	Permanent.
Original water.....	70.5°	39.6°
(3) After passing aluminum chute.....	70.5°	39.0°
(4) After passing aluminum tube.....	70.5°	39.0°

The next question that suggested itself was to ascertain whether direct sunlight would have any considerable influence on the results.

Experiments Nos. I. and II. were therefore repeated, the apparatus being arranged exactly as described, but exposed on the flat roof of the laboratory to direct sunlight. The time was 11 to 12 in the forenoon, and the sun shining brightly. The velocity of flow was 1 litre in 6 minutes.

Experiment IV. in bright sunlight.	Hardness (French scale) by soap solution.	
	Total.	Permanent.
Original water.....	63°	45.6°
After passing aluminum chute.....	62.5°	40.2°
After passing aluminum tube.....	63°	42°

It was now decided to introduce a new factor into the experiments by adding aluminum sulphate with the object of discovering whether this would react as usual with a hard water by converting the carbonates of lime and magnesia into sulphates, and if so, would its action be retarded by passing the water so treated down the

sults obtained in Table I. The soluble calcium has been increased by the alum 7 or 8 times, whilst the insoluble has nearly all been removed by boiling and filtering off the residual insoluble carbonates.

Further experiments were conducted as tabulated in Table II., the first being a repetition of those in Table I., but the speed being increased to 1 litre in 3 minutes. The second group with the previous addition of alum, but without final boiling. The third group of experiments were conducted on a water of a very different composition, without the use of alum.

The effect of the previous treatment of the water with alum is again manifest in the reduction of insoluble calcium and the increase of the soluble calcium, the latter again showing an increase over the water not "alumed" of 6 to 7 times.

Conclusions.—Reviewing the results, comparing the water passed over the aluminum chute or through the tube, and considering the claims made that water so treated forms a different deposit from that untreated, we should expect to see a difference in the salts, thus separated on evaporation. But it is evident that in none of the tests do we get a very considerable reduction or increase in the resultant salts, either in the "ionic" state or as combined salts on evaporation. In Table I. there is apparently a tendency to convert some of the calcium, which would ordinarily be soluble, to the insoluble form; i. e., from permanent to temporary hardness. This effect is confirmed in the first group of Table II. But in the second group of experiments

(Table II.) when using aluminum sulphate, the action of the aluminum metal does not appear to have exercised any inhibiting on the usual action of the alum, and in the third group (Table II.) when using a water from Austin of a very different kind, without the addition of alum, the effect of the passage over metallic aluminum was apparently the opposite of what it showed in the other water, namely, to convert insoluble to soluble calcium; i. e., from temporary to permanent hardness, yet great care was taken in the manipulations and extractions, and the results are undoubtedly comparative. In the addition of alum the usual expected change is marked decisively, yet there is nothing to indicate the passage over the metallic aluminum.

The tests do not show that there is any marked difference between passage in daylight or darkness, the other essentials, such as disposition due north and south, having been carefully complied with.

If carbon dioxide is supposed to be rapidly evolved, surely this would have some effect on the steel above

doing no good whatever. Scale was forming in the boilers apparently at the same rate as before the "luminator" was installed. He also knew of other cases where the results had been equally unfavorable. On the other hand, there were instances within his knowledge where the "luminator" was being used to treat waters of which the hardness was mainly temporary, in which it was stated to be working quite successfully, causing the calcium carbonate to deposit in the boiler in a loose pulverulent form instead of an adherent scale. He had not seen these particular "luminators" at work himself, but the facts were well authenticated by other chemists whom he knew personally. It was quite certain that by passing over the "luminator" the water was not softened in any way, the only change being a slight reduction in the amount of free carbon dioxide. He could confirm Mr. Lake's results in this respect. Thus, in two cases he had tested samples of water before and after passing the "luminator." The first case was one in which the "luminator" was said to be treating successfully

TABLE II.

	Hardness by soap solution Total. Permanent.	Mineral analysis, parts per 100,000.							
		Ionic estimations.				Combinations on evaporation.			
		Insoluble.		Soluble.		Insoluble.		Soluble.	
		Cal- cium.	Mag- nesium.	Cal- cium.	Mag- nesium.	Calc. carb.	Magnes. carb.	Calc. sulph.	Magnes. sulph.
Experiment VI.		Velocity of flow equals 1 litre in 3 minutes.							
Original water (tap water from laboratory)	52.0 42.8	8.70	1.47	0.36	6.20	21.75	5.09	1.22	30.63
(10) Passed chute.....	56.0 40.0	8.80	1.30	0.19	6.06	22.00	4.50	0.65	29.94
(11) Passed tube.....	54.0 40.0	8.73	1.30	0.22	5.98	21.82	4.50	0.75	29.54
Al ₂ (SO ₄) ₃ added, equivalent to 3 parts per 100,000.		Velocity of flow equals 1 litre in 3 minutes.							
Original water.....	52.0 39.0	7.25	1.53	1.49	5.33	18.13	5.29	5.07	26.33
(12) Passed chute.....	52.0 40.8	7.22	1.38	1.61	5.41	18.05	4.77	5.47	26.73
(13) Passed tube.....	54.0 39.4	7.42	1.31	1.36	5.60	18.55	4.53	4.62	27.66
"Austin" water.		Velocity of flow equals 1 litre in 3 minutes.							
Original water.....	43.4 14.6	10.6	2.03	0.28	1.54	26.50	7.02	0.95	7.61
(14) Passed chute.....	40.8 15.4	10.35	1.78	0.52	1.63	25.88	6.16	1.77	8.05
(15) Passed tube.....	39.2 16.4	10.42	1.73	0.30	1.63	26.05	5.99	1.02	8.05

the water line in a boiler, where we often get serious "pitting," and surely zinc plates are hardly employed as scale detergent, but rather to inhibit "pitting" action, and any detergent action is only incidental to the resulting zinc salts in solution.

All chemists and engineers experienced in hard water troubles are eagerly watching for any improvement in the methods of water softening, and would welcome any method so very simple as passing water over aluminum plates which would even prevent the scale adhering, but the process seems to be of little value, even if this can be effected (which seems very doubtful), unless the resulting acid gases and sludge can be removed, which appear to cause corrosion and overheating of the plates, with subsequent "pitting" and "bulging" where the sludge is excessive.

DISCUSSION.

Mr. L. Archbutt said he was afraid the "luminator" had not been the unqualified success which one would gather from reading the paper to which Mr. Lake had referred. It was very difficult to get at the true facts. His personal experience extended to only one apparatus, which was at the present time being used to treat a water of 34° total hardness and 19.4° alkalinity. The "luminator" had been at work on this water for several weeks, but up to the present appeared to be

a water from the oolite. This water gave the following results:

	Before "luminator."	After "luminator."
	Grains per gallon.	
Alkalinity as calcium carbonate...	20.30	20.30
Free carbon dioxide.....	1.7	1.4

In the second case the "luminator" was working unsuccessfully on the water he had previously referred to, and the results were:

	Before "luminator."	After "luminator."
	Grains per gallon.	
Lime (CaO)	11.73	11.87
Magnesia (MgO).....	5.06	5.21
Hardness, degrees.....	33.5	34.1
Alkalinity as CaCO ₃	19.35	19.35
Free carbon dioxide.....	1.50	1.15

In Neff and Brandes' original patent there was no reference to the prevention of scale in boilers, but it was stated that the water after flowing over aluminum has wonderful cleansing properties and is enabled to wash soiled linen in a much shorter time than the untreated water. A friend of his who had made careful tests to prove the truth or otherwise of this assertion failed to obtain slightest evidence of any new properties acquired by the water.

The manner in which this apparatus had been boomed and the exaggerated statements made in regard to it had made him, perhaps, unduly skeptical.

He could not disbelieve what his friends told him as to the remarkable effects produced on chalk waters in changing the character of the deposit formed in boilers, but he was entirely skeptical as regards the suggestion that this was due to particles of aluminum acting as nuclei. A more likely explanation was contained in Mr. Jerome Alexander's remarks on Mr. Duncan's paper.

Mr. Law said the action of the "luminator" might perhaps be more physical than chemical.

Dr. Sand agreed and said that if a very small amount of aluminum hydroxide were formed in the water by the "luminator" treatment in the state of colloidal solution, it would undoubtedly be deposited with the scale and might conceivably alter the mode of precipitation and the mechanical properties of the scale completely.

Mr. Wilke asked whether any other grooved surface would answer as well.

Mr. Timmans asked whether the organic content of the water was affected by the treatment.

Mr. Archbutt said, in answer to a question by Mr. Duncalfe, that the combined carbon dioxide was not affected appreciably by the treatment. In reply to a question by Mr. Wood, he said the treatment would probably aerate the water. The questions of Messrs. Wilkie and Timmans he was unable to answer from personal knowledge. The makers lay great stress on the importance of keeping the aluminum surface bright, for which purpose it had to be cleaned frequently with acid followed by rubbing with emery cloth; in some cases the surface is then washed with caustic soda.

SILOXYD GLASS.

The U. S. Consul General at Zurich, Switzerland, reports the discovery by a Zurich inventor of a method of producing suitable apparatus for the chemical industry from electrically melted quartz.

According to the U. S. Consular Report, from which these notes are taken, the product is an improvement on quartz gut, or quartz glass, and is especially suited to the manufacture of pipes, tubes, receptacles, flasks, muffles, and other articles used in the production of chemicals, required to withstand a very high temperature and at the same time the effect of concentrated acids. Most of the articles used for such purposes have, until recently, been made of platinum, for the reason that a quality of glass that would meet the requirements had not been produced.

Articles made by the new process from electrically fused quartz because of the low coefficient of expansion, can be subjected to extreme changes of temperature without damage. It is now possible to make articles of large dimensions of this glass, such as socket pipes, acid bottles, and other vessels, that will hold as much as 25 gals. This new material has been placed upon the market as "siloxyd" glass, and the process of manufacture has been patented in most of the European countries and in the United States.

Quartz glass, which has long been recognized as an important material in the manufacture of various articles employed in the chemical industry, and for which "siloxyd" is now being substituted where a severe test of temperature is required, was first discovered in 1839 by Prof. Gaudin, who later produced from the same material some tubes and elastic threads which were exhibited at the Paris Exposition in 1878.

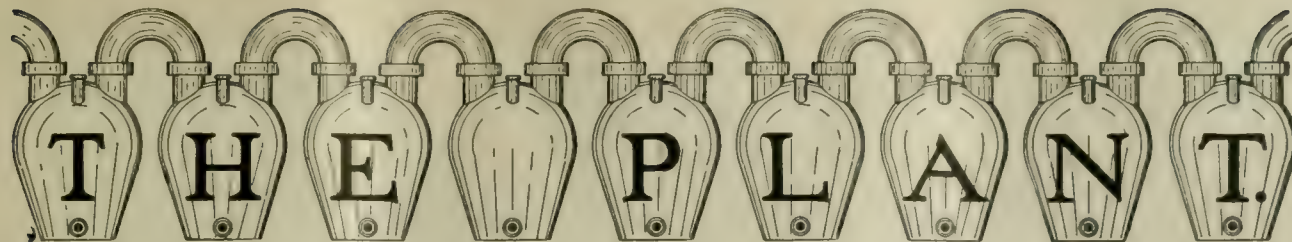
In 1889, Boys, who saw the possibilities of this remarkable substance, succeeded in making from quartz small tubes and other articles. Although there were many subsequent experiments, little progress was made in the development of the quartz-glass industry until 1900, when Hereaus and Achendstone succeeded in making clear rock-crystal objects of sufficient size for scientific and mechanical purposes.

The raw material from which the glass is produced is washed quartz sand containing 95 per cent silicic acid, which is melted in an electric furnace in which the temperature rises to 2,000° F. All the agencies known to the glass-working industry, including air, steam, gases, etc., can be applied, and it is now possible to melt and to mold into almost any desired form as much as 50 pounds of quartz. A remarkable quality of the quartz produced by the thermoelectric process is its resistance to acids. Even boiling acid, with the possible exception of hydrofluoric or phosphoric, will not corrode it. Quartz has the advantage of a coefficient of expansion about one-seventeenth that of the best glass suitable for chemical utensils and apparatus.

The chief objection to pure quartz glass as a material for apparatus used in the chemical industry is that it becomes brittle at high temperature, passing from the amorphous to the crystalline state with a diminution of strength. Until the discovery of Dr. Wolf-Burckhardt, authorities on the subject claimed that the addition of any other ingredient to the raw material would injuriously affect the quality of the melted quartz.

The new process consists in adding to the raw quartz solutions of oxides of zircon, titanium, and other metals difficult to fuse (or silicates of same to silicic acid), the resulting mixture giving on fusion a transparent glassy substance which fuses at a temperature of 1,750°. The advantages claimed for this material over ordinary quartz glass are that its strength is 30 to 50 per cent greater than "quartz gut," tested by bending, and 10 to 30 per cent more tested by pressure, and that it is less brittle, because the devitrification is only about half that of quartz glass. It is also more resistant to basic metallic oxides.

The superior advantages claimed for "siloxyd" glass give to this new material a wide range of usefulness, especially for apparatus used in the acid industry and for laboratory purposes where socket pipes, tee pipes for acid conduits, evaporating basins, concentrating dishes, cooling vessels, special boxes, conical pipes, condensation utensils, balls for acid towers, etc., are required.



THE MANUFACTURE OF AQUA AMMONIA AND SAL-AMMONIAC DIRECT FROM RAW GAS LIQUOR.

By R. W. HILGENSTOCK.*

The accompanying illustrations show an arrangement for the manufacture of aqua ammonia and sal-ammonia direct from raw gas liquor. The raw gas liquor, which comes from gas works or coke-oven

plants with recovering of by-products is pumped into the overhead feed regulating tank (6) by pump (19), from where it flows into the upper section of the pre-heater or carbonic acid extractor (1). The three upper rings of this apparatus are provided with lead cooling coils in order to keep the liquor cold, so that it can absorb again any particles of ammonia, that should be driven off from the heating chambers below. The liquor travels down from section to section; before it enters the upper rectangular treating chamber, however it is brought into the lower section of the cooler (3), where it is supposed to cool the ammonia vapors coming from the still (2), but at the same time is heated up to about 80° C., and goes back now in the upper heating chamber of apparatus (1). In the three heating chambers the liquor is gradually heated up to about

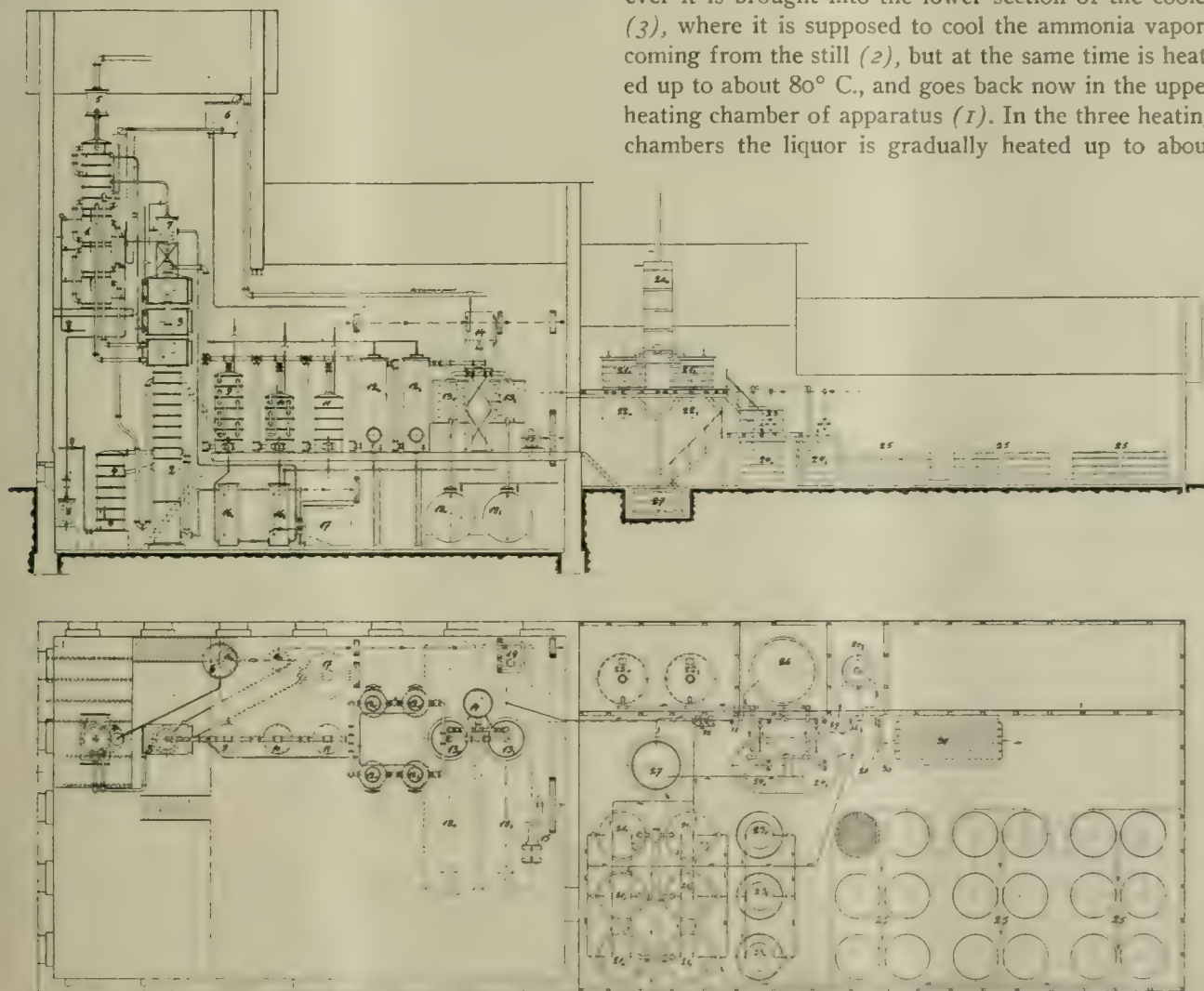


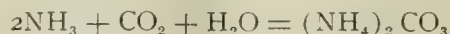
Fig. 1—Plan and Longitudinal Section of Plant Showing Arrangement of Apparatus.

- | | | |
|-------------------------------------|--|---|
| 1 Separator for CO ₂ . | 12 Bone char filler. | 23 Supply vessel for hydrochloric acid. |
| 2 Principal column separator. | 13 Primary absorption vessel. | 24 Filler tank. |
| 3 Dephlegmator. | 14 Secondary absorption vessel. | 25 Neutralization tank. |
| 4 Lower column. | 15 Steam engine. | 26 Crystallization tank. |
| 5 Scrubber. | 16 Cast iron catch basin. | 27 Same as (26). |
| 6 Regulator to draw off gas liquor. | 17 Vessel to prepare milk of lime. | 28 Mixing tank. |
| 7 Steam boiler. | 18 Supply vessel for ammonium chloride liquor. | 29 Draw off tank. |
| 8 Distilled water cooler. | 19 Pump for gas liquor. | 30 Inflow to scrubber 29. |
| 9 Water washer. | 20 Scrubber. | 31 Centrifuge. |
| 10 Soda washer. | 21 Concentration tank. | 32 Drying apparatus. |
| 11 Oil washer. | | 33 Pump. |

100° C. The arrangement of the whole apparatus permits one to work with this high temperature without any loss in ammonia, and it is clear that a high percentage of carbonic acid and sulphuretted hydrogen are driven off, which means an enormous saving of lime in the later process. The reader will see, from Table I, in what quantities ammonia, carbonic acid and sulphuretted hydrogen are contained in different gas liquors:

taken, that only a certain quantity of water is brought into this apparatus; it must be sufficient to absorb enough ammonia for retaining carbonic acid and sulphuretted hydrogen. To understand the reactions which take place I give the formulas below:

1. For carbonic acid:



Or



TABLE I.

Name.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Specific gravity.....	1.020	1.024	..	1.026	1.019	1.025	1.025	..	1.033
Cyanides.....	*	..	..	*	..	*	..	*	*
Ferrocyanides.....	*	..	..	..	..	*	*	..	*
Chloride as MCl.....	0.006	0.620	..	0.685	0.12	*	..	*	0.946
Ammonia, total.....	1.827	2.630	1.84	2.476	1.382	1.593	1.550	1.316	2.745
Ammonia, fixed.....	0.110	0.395	1.28	0.490	0.120	0.100	0.100	0.116	0.600
Ammonia, volatile.....	1.717	2.235	1.56	1.986	1.262	1.493	1.450	1.200	2.145
Carbonic acid.....	1.860	2.023	1.39	2.019	1.493	1.819	1.830	1.485	2.365
Sulphuretted hydrogen.....	1.6256	1.634	0.397	0.629	0.100	0.068	0.064	0.093	0.709
Sulphur, total.....	0.6331	0.695	..	0.750	0.1366	..	..	..	0.863
Sulphur in per cent sulphate.....	4.140	0.59	..	0.43	4.03	..	..	..	0.81
Sulphur in per cent rhodanid.....	2.223	7.91	..	14.40	16.47	..	..	..	12.91
Sulphur in per cent trosulphate.....	0.55	5.66	..	6.24	10.83	..	..	..	8.94
Sulphur in per cent sulphide.....	93.05	85.83	..	78.93	68.67	..	..	..	77.33

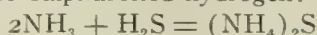
*Trace.

The liquor, after leaving the lower heating chamber of apparatus (1) enters the top section of the still (2), travels down section for section and coming in contact with always hotter steam on its way downwards; the last particles of carbonic acid, sulphuretted hydrogen and the whole "volatile ammonia" are set free in these upper sections. To recover, also, the ammonia compounds, which are not decomposed by heat, milk of lime from apparatus (17) is pumped into the high vessel below these sections and thoroughly mixed with the liquor by steam. This mixture of milk of lime and gas liquor then flows into the secondary part of still (2) where it is boiled up again with live steam, to drive off the last particles of ammonia. The waste liquor, leaving this part of the still, does not contain more than 0.005 per cent NH_3 . The sections of the secondary still and those of the primary are entirely the same.

For the settling of the time in the waste-liquor, large settling-basins, made in heavy concrete are provided and the overflows are arranged so that the liquor has to travel a long way in order to give the lime ample time to settle; at the end of this purifying plant the liquor is absolutely clear, so that it can be piped into the city sewer.

Let us now return to the still (2). The ammonia-vapors, containing also carbonic acid and sulphuretted hydrogen, which are set free in the different sections of the still, travel upwards into the cooler (3) of special construction, which serves the purpose to retain most of the steam vapors that are carried up by the ammonia, the condensed steam vapors flow back into the upper section of the still, while the ammonia gases leave the cooler comparatively dry, but still contain a certain percentage of carbonic acid and sulphuretted hydrogen. To remove these impurities, the ammonia gases are washed with aqua ammonia in a so-called water washer (9); however care must be

2. For sulphuretted hydrogen:



Or

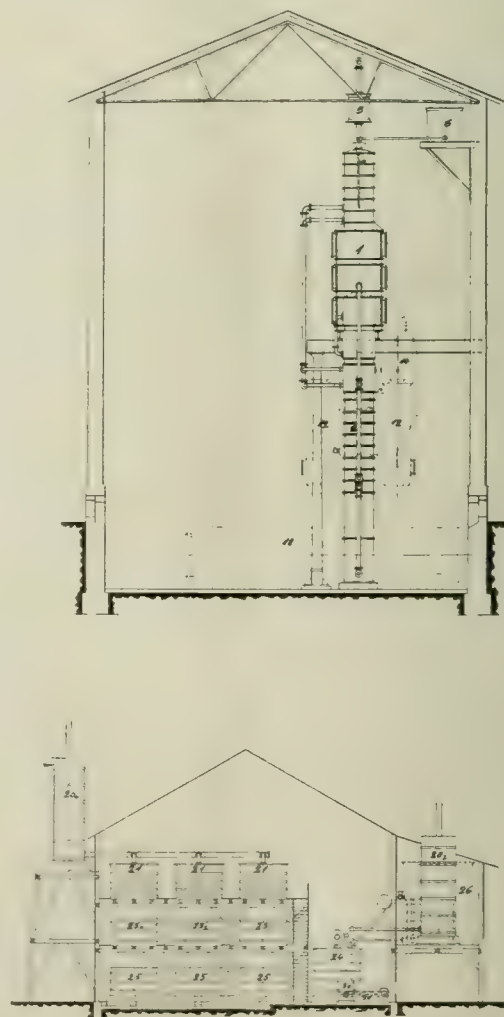
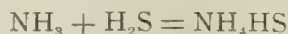


Fig. 2—Side Elevation of Plant.

To be absolutely sure, that even in unregular operation no carbonic acid can pass into the filters, which would also mean stoppage of the pipes and fittings, a further smaller washer (10) is provided, filled with a solution, containing about 20 per cent of caustic soda; carbonic acid and sulphuretted hydrogen would combine with the soda to carbonate of soda or sodium sulphide; both compounds are soluble in water. At the same time, however, the washer serves the purpose, to further dry the ammonia gases, as some of the moisture, which is carried mechanically along will be retained by the soda. To relieve the gas from oily and tarry substances, an oil washer (11) is installed, which is filled with a heavy mineral or paraffin oil.

From now the further process is exactly the same as I have described in an article in the January issue of this paper, so it is not necessary to repeat it. The finished aqua-ammonia, however, is supposed to have 17 to 20 per cent NH_3 only; the reason for this will be seen below. For the convenience of the reader I give Table II, showing the specific gravity of the aqua-ammonia at different strengths:

TABLE II.

Spec. gravity at 15° cels. —1.	Per cent NH_3 by weight.	Grammes of NH_3 in 1 liter.	Spec. gravity at 15° cels. Water at 15° cels. = 1.	Per cent NH_3 by weight.	Grammes of NH_3 NH_3 in 1 liter.
1.000	0.00	0.0	0.960	9.91	95.1
0.998	0.45	4.5	0.958	10.47	100.3
0.996	0.91	9.1	0.956	11.03	105.4
0.994	1.37	13.6	0.954	11.60	110.7
0.992	1.84	18.2	0.952	12.17	115.9
0.990	2.31	22.9	0.950	12.74	121.0
0.988	2.80	27.7	0.948	13.31	126.2
0.986	3.30	32.5	0.946	13.88	131.3
0.984	3.80	37.4	0.944	14.46	136.5
0.982	4.30	42.2	0.942	15.04	141.7
0.980	4.80	47.0	0.940	15.63	146.9
0.978	5.30	51.8	0.938	16.22	152.1
0.976	5.80	56.6	0.936	16.82	157.4
0.974	6.30	61.4	0.934	17.42	162.7
0.972	6.80	66.1	0.932	18.03	168.1
0.970	7.31	70.9	0.930	18.64	173.4
0.968	7.82	75.7	0.928	19.25	178.6
0.966	8.33	80.5	0.926	19.87	184.2
0.964	8.84	85.2	0.924	20.49	189.3
0.962	9.35	89.9	0.922	21.12	194.7

THE MANUFACTURE OF SAL-AMMONIAC.

Sal-ammoniac is formed by the chemical combination of one part of ammonia (NH_3) with one of dry hydrochloric acid (HCl). The aqua-ammonia, as it leaves the absorbing vessels at a strength of 17 to 19 per cent NH_3 , is mixed with sufficient muriatic acid, containing about 33 per cent dry hydrochloric acid (HCl) until a slightly alkaline solution is obtained; this solution is concentrated by boiling and after filtering is drawn into crystallizing tanks, where the sal-ammoniac crystals form. These crystals are taken out and dried, while the mother liquor, after having been mixed with fresh *neutralized* liquor, goes back into the boiling tanks, where it is again concentrated.

At 15° Cels. a saturated solutions of sal-ammoniac

(NH_4Cl) specific gravity 1.077, contains about 26.25 per cent NH_4Cl . When 100 lbs. of concentrated ammonia liquor of 17 per cent NH_3 (therefore containing 17 lbs. NH_3) are treated with muriatic acid, 36.4 lbs. of dry hydrochloric acid (HCl) are needed for neutralization; as chemically pure muriatic acid of 21½° Bé contains 36.4 per cent HCl , 100 lbs. of same will be required to neutralize 100 lbs. of 17 per cent aqua-ammonia, as commercial muriatic acid of 20½° Bé (containing about 33 per cent HCl instead of 36.4 per cent) is generally used, 110 lbs. of same are necessary to neutralize 100 lbs. of 17 per cent aqua-ammonia, forming $17 + 36.4 = 53.4$ lbs. sal-ammoniac (NH_4Cl).

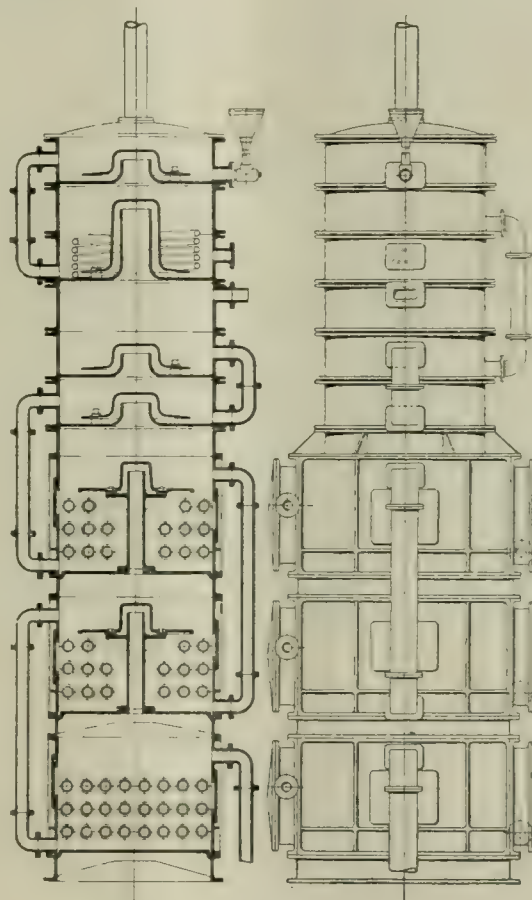


Fig. 3—Section Through Pre-heater or Carbonic Acid Extractor.

The neutralizing tanks in which aqua-ammonia and muriatic acid are mixed, are made of wood and have a lining of hard burned clinkers, laid in sulphur and glass dust. The dimensions depend on the desired daily production of crystals, but they must be of ample size to supply the boiling and crystallizing tanks if for any reason the supply of aqua-ammonia or muriatic acid may be temporarily stopped. The inlet pipes for aqua-ammonia and muriatic acid are either made of hard rubber or earthenware; the latter are preferable because hard rubber will become soft in a comparatively short time. A paddle, made also from earthenware is supposed to mix the two liquids thoroughly; care however, must be taken that the neutralization process is very slow, as considerable chemical

heat would be created when ammonia and hydrochloric acid combine too fast. The writer experienced several explosions, due to this circumstance. When neutralizing, samples of the mixed liquor must be taken; it is always preferable to have the solution slightly "acid" in order to prevent losses of ammonia. (As the solution becomes warm, there would doubtless be ammonia vapors escaping when the solution would be "alkaline.") It is furthermore preferable, to draw the chloride of ammonia vapors through an

(American pitch pine) and lined with hard burned clinkers, laid in best Portland cement. A lead, or better, a cast iron steam coil heats the neutralized liquor; by evaporation this is concentrated until a distinct white skin is swimming on top, which shows that the solution is properly saturated; measured with a hydrometer, it would indicate about 10° Bé at 96° to 98° Cels. For information I give Table III, showing the specific gravity of sal-ammoniac solutions at different concentrations:

TABLE III.

Spec. gravity.	Per cent NH ₄ Cl.	Spec. gravity.	Per cent NH ₄ Cl.
1.00316	1.0	1.04325	14.0
1.00632	2.0	1.04524	15.0
1.00948	3.0	1.04804	16.0
1.01264	4.0	1.05086	17.0
1.01580	5.0	1.05367	18.0
1.01880	6.0	1.05648	19.0
1.02180	7.0	1.05929	20.0
1.02481	8.0	1.06204	21.0
1.02781	9.0	1.06479	22.0
1.03081	10.0	1.06754	23.0
1.03370	11.0	1.07029	24.0
1.03658	12.0	1.07304	25.0
1.03947	13.0	1.07375	26.0

In case the plant is built near the residence district of a city, the escaping vapors of these concentrating tanks are passed through a tower scrubber, filled with coke, to remove the bad smell.

The saturated liquor is drawn from the concen-

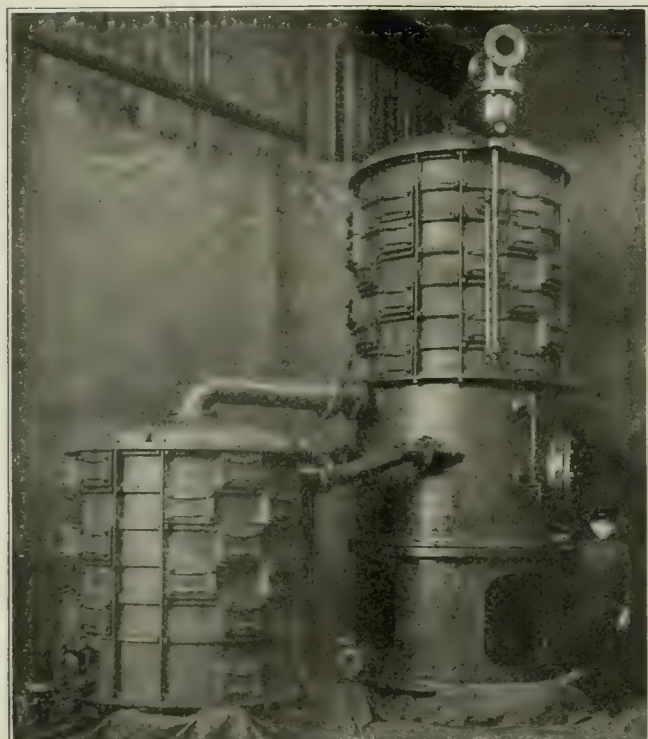


Fig. 4—Primary and Secondary Still.

earthenware scrubbing tower; the washing fluid can be pumped over and over again, until it contains a certain percentage of NH₄Cl, and is worked up with the other liquor in the operation.

When the neutralizing tanks are filled to a certain height, the flow of muriatic acid is stopped and only aqua-ammonia is led in until a sample, to which one or two drops of a solution of methyl orange are added, shows a wine yellow color. The liquor is now drawn off by means of a rubber hose into the receiving tank, where it is mixed with the mother liquor, obtained from the crystallizing tanks.

The receiving tank is a plain wooden vessel. If a sample of the neutralized fluid mixed with mother liquor from the crystallizing tanks show a red color when a few drops of methyl orange are added (thus indicating an acid solution) some more ammonia must be added, as a "sour" solution will badly attack the pumps and the coils in the concentrating tanks (see below). After having made sure that the fluid is properly neutralized, it is pumped into the concentrating tanks.

The concentrating tanks are made of wood

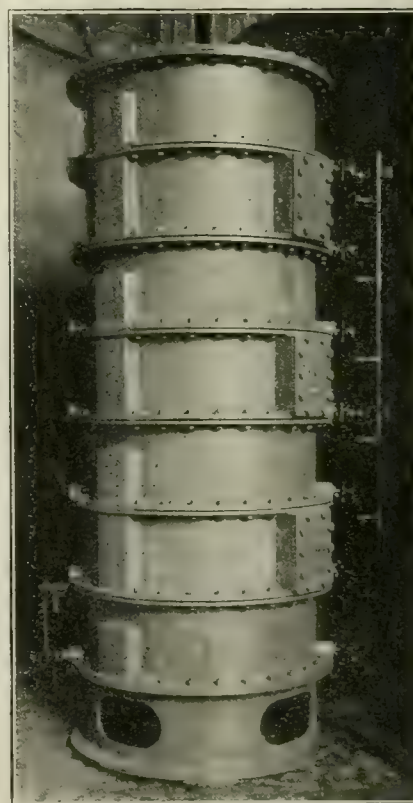


Fig. 5—Oil Washer.

trating tanks through a short rubber hose into the filter tanks.

The filter tanks are also made of wood, preferable American pitch pine and are provided with a false wooden bottom, on which bone black of different size

is piled, on top of the bone black is a filter cloth. To avoid crystallization in the bone black, a small steam coil is arranged to keep the liquor hot.

The crystallizing tanks. The filtered liquor flows through a square trough, then into one of the crystallizing tanks, built also from American pitch pine wood.

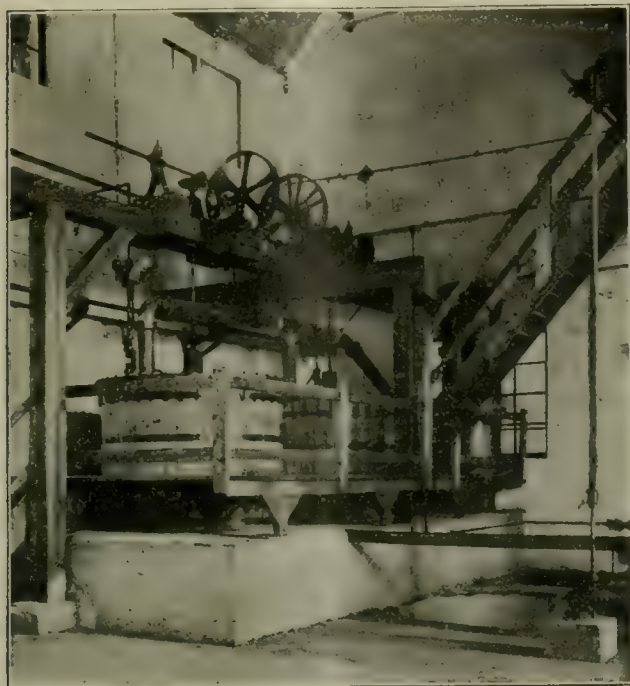


Fig. 6—Neutralizing Tanks.

The liquor cools in these tanks; after its temperature has dropped sufficiently and the crystals have formed, the mother liquor is drawn off through a 2-in. outlet at the bottom of the tanks into a square wooden trough and used over again in the receiving tank as described above.

Drying process. The fine white crystals, which have formed on the walls, crystallizing sticks and bottom, are taken out and partly dried in a centrifugal extractor, but as the moisture can in this manner only be reduced to $1\frac{1}{2}$ to 2 per cent, the crystals must afterwards be dried on a drying table. Glazed terra cotta tiles are laid on small brick piers in very rich clay; the crystals must be continuously turned over while being dried, as otherwise they will bake together, as well as to the drying table. The heat is furnished by the exhaust steam from the coils in the concentrating tanks. When the crystals are dry, they are packed in casks and barrels and are then ready for shipment. Pure sal-ammoniac crystals are white. They may vary in size from fine powder to granulated sugar crystals. Commercial sal-ammoniac has a color varying from gray to a light brown, this being due to iron compounds and other impurities contained therein.

DATA.

I will give now some data and figures obtained in actual experience and shall start with the production, yields and consumption of muriatic acid and concentrated liquor. Owing to the immense quantities of

liquids that were in operation, it was often very hard to get an average analysis. One-tenth of one per cent difference would make the yields climb up to over 100 per cent, as will be seen in Table IV:

During February no regular work could be done due to an explosion outside the building, which did heavy damage to the steam and acid pipe lines leading into the building. In general operation a loss of 6 to 10 per cent, both on acid and ammonia may be expected.

In Table V I give the manufacturing and operating expenses for a plant, producing about 6,000 to 6,500 lbs. of crystals per day of 12 hours:

TABLE V.

Month.	Production in pounds.	Total expense.	Per 100 pounds production.	Mfg. expense, not incl. repair of casks and barrels, and repair work.	Per 100 pounds production.	Labor for operation.	Per 100 pounds production.	Repair of casks and barrels.	Repair on apparatus and machinery.
Jan.	172,979	\$383.61	17.9c	\$310.22	16.9c	\$166.90	9.6c	\$73.39	\$
Feb.	145,526	305.60	20.4c	241.43	16.6c	130.47	8.9c	64.17	17.53
Mar.	265,980	338.16	12.8c	248.31	10.8c	152.52	5.7c	72.12	17.26
Apr.	198,000	325.94	16.4c	233.86	11.8c	171.19	8.1c	74.82	17.26
May	146,465	321.93	21.9c	225.31	15.3c	144.27	9.8c	77.68	18.94
June	165,644	338.64	20.5c	240.33	14.5c	157.34	9.5c	90.89	17.52
July	118,466	317.65	26.8c	245.25	20.7c	156.65	13.2c	65.35	7.05
Aug.	198,814	367.38	17.8c	285.32	14.3c	173.42	8.7c	70.60	11.46
Sep.	158,106	319.74	20.2c	245.94	15.5c	153.59	9.9c	65.10	8.70
Oct.	130,909	318.79	24.3c	266.51	20.3c	181.49	13.8c	38.66	13.62
Nov.	163,528	302.05	18.4c	238.83	14.6c	141.61	8.6c	62.57	1.65
Dec.	161,938	308.37	19.0c	232.47	14.3c	134.37	8.3c	68.40	7.50
Average		20.4c		15.5c		9.5c			

As to the repair work on casks and barrels, I want to say, that they were bought "second hand" and had to be washed, dried and fixed up again before they could be used for shipment. A small cooper shop in which this kind of work was done was attached to the building. In spare time the cooper had to help in nailing up casks and barrels after they had been filled.



Fig. 7—Outside View of Building.

To determine the amount of crystals contained in the liquor in the different tanks, an analysis was made for the percentage of NH_3 ; having this figure one was able to calculate the total NH_4Cl contained in the

liquor. Table VI shows some analyses of the different solutions:

TABLE VI.				
Neutralizing tanks.	Receiving tanks.	Concentrating tanks.	Filter tanks.	Crystallizing tanks.
Per ct. NH ₃ .	Per ct. NH ₃ .	Per ct. NH ₃ .	Per ct. NH ₃ .	Per ct. NH ₃ .
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
8.86	8.93	11.48	11.40	11.35
8.00	8.65	11.50	11.46	11.45
8.62	9.00	11.92	11.88	11.80
8.54	9.13	11.60	11.50	11.43
8.40	8.98	11.83	11.75	11.73

Commercial sal-ammoniac may contain 98 per cent

of NH₄Cl, slight traces of iron and sulphuric acid and about 1.5 to 2.0 per cent moisture.

For fine white sal-ammoniac, as it is used for batteries, etc., however, the specifications are much more rigid. As a rule, the following is asked for: Chloride of ammonia must contain only traces, if any, of matter insoluble in water; it must not leave more than a trace of residue when 5 grammes are heated in a platinum capsule over a low Bunsen flame until white fumes cease to be involved and must give little or no

TABLE IV.

Month.	Part of month.	Production.	Muriatic consumed about 32 per cent HCl.	Liquor consumed.	Equals NH ₃ .	Yield NH ₃ .	Yield HCl.	Number of work days.	Average daily product.
January	1-11	54,260	138,643	102,094	19,760	82.0	83.4		
	11-21	60,700	138,856	113,478	21,092	91.5	93.2		
	21-1/2	58,010	162,481	144,538	26,213	70.3	76.1		
Total		172,979	439,980	360,110	67,065	81.2	84.2	31	5,578
February	1-11	63,150	139,456	157,410					
	11-21	52,450	98,600	110,000	11,602	43.0	28.4		
	21-1/3	29,920	26,398	14,708	4,674	202.4	241.5		
Total		145,526	264,454	282,118	16,276				
March	1-11	117,429	193,629	213,397	41,044	91.0	129.2		
	11-21	73,551	199,365	100,026	17,279	135.0	78.7		
	21-1/4	75,317	198,323	144,777	27,516	81.0	81.0		
Total		265,980	591,317	458,200	85,839	102.3	96.3	31	8,580
April	1-11	78,646	157,546	123,684	24,420	102.3	106.4		
	11-21	42,654	119,111	96,062	19,701	68.8	76.4		
	21-1/5	77,006	172,144	124,256	22,829	107.1	95.3		
Total		198,000	448,801	344,002	66,950	92.7	92.7	28	7,070
May	1-11	47,480	114,823	22,434	3,525	106.2	88.2		
	11-21	33,335	165,699	123,406	22,799	46.5	42.9		
	21-1/6	45,650	118,763	75,068	13,382	108.4	82.0		
Total		146,465	399,285	220,708	39,706	87.0	71.0	26	5,633
June	1-11	49,917	136,764	34,168	6,750	91.2	77.8		
	11-21	77,354	145,427	115,992	21,240	113.4	115.7		
	21-1/7	38,373	128,093	137,149	24,871	63.9	49.1		
Total		165,644	410,284	187,309	52,861	89.5	80.8	28	5,915
July	1-11	32,970	67,321	50,432	9,159	114.3	104.4		
	11-21	35,123	145,745	92,157	17,192	64.9	51.4		
	21-1/8	50,373	137,828	140,097	24,292	65.9	78.2		
Total		118,466	350,894	282,686	50,643	81.7	78.0	28	4,230
August	1-11	56,626	110,800	90,251	16,078	111.9	108.7		
	11-21	51,713	171,812	134,190	13,630	66.5	64.2		
	21-1/9	90,475	180,020	136,387	23,748	121.0	107.2		
Total		198,814	462,632	360,828	53,456	99.8	93.3	29	6,850
September	1-11	45,397	136,763	102,897	17,678	70.7	81.5		
	11-21	37,144	107,972	77,221	16,761	73.3	70.4		
	21-1/10	75,577	177,141	119,045	21,885	109.7	91.0		
Total		158,100	421,876	299,163	56,324	84.6	80.9	26	6,080
October	1-11	22,257	60,531	54,848	10,087	70.1	78.4		
	11-21	52,419	143,944	110,909	21,477	77.2	77.7		
	21-1/11	56,233	130,676	107,705	20,694	86.3	91.8		
Total		130,909	335,151	273,462	52,258	77.8	82.6	26	5,030
November	1-11	58,367	122,821	94,803	19,015	97.5	101.3		
	11-21	47,359	119,072	94,858	18,004	83.6	84.8		
	21-1/12	57,802	126,120	75,003	18,568	98.9	97.7		
Total		163,528	368,013	264,664	55,587	93.3	94.6	26	6,320
December	1-11	64,255	136,912	86,926	19,464	104.9	100.1		
	11-21	49,681	107,633	67,194	18,614	84.8	98.4		
	21-1/1	48,002	89,421	87,132	15,376	92.7	114.5		
Total		161,938	333,966	241,252	53,454	94.1	104.3	27	6,220
						89.5*	86.9*		

*Equals average for twelve months.

miliness, showing presence of sulphate of ammonium, when dissolved in water and hydrochloric acid and barium chloride are added. The size of crystals must be very fine and uniform.

As to the building in which the sal-ammoniac is placed, I want to say, yet, that iron work should be avoided as much as possible, because the sal-ammoniac vapors are very corrosive and would destroy the iron in a short time. The best material is wood and wooden timbers soaked in creosote or the like. Wherever platforms are built, it is advisable to make a floor of hard burned clinkers, the joints to be filled out with hot asphalt mixed with screened sand. The room for the crystallizing tanks should be high and airy, so that the hot liquor can cool off quickly, especially in hot summer days.

According to a U. S. Consular Report 12 large paper manufacturing concerns in the eastern portion of the United States, having an organization center in Boston, have joined in the formation of a Philippine corporation which will purchase and handle for these manufacturers hemp and hemp by-products now to be had in the Philippines. The capital of the company in the Philippines is placed at \$150,000 gold, but it is stated by the incorporators that a large amount of capital is back of the venture. The stock in the new concern is all held by paper manufacturers, and they expect to use the company's entire output in their own establishments in the United States. American machinery has already been imported to some extent and more has been ordered. Eventually a pulping factory will be established in Manila to utilize such supplies of hemp as may be purchased in the field or in an unmanufactured state, but for the present the company expects to devote its energies to the purchase of hemp which has been prepared on special machines designed to use the whole hemp plant.

In 1911, according to B. S. Butler, of the U. S. Geological Survey, the mines of Michigan produced 219,840,102 pounds of copper, valued at \$27,480,013, and 497,281 fine ounces of silver, valued at \$263,559, a total value for both metals of \$27,743,572. This is a decrease in value of \$715,698, or about 2.5 per cent, from the 1910 production, due to a slightly smaller output of copper and a little lower average price for the metal. Owing to this slight decrease in the price of copper there was a decline from \$2.54 in 1910 to \$2.50 in 1911 in the average value per ton of rock treated. The recovery of refined copper per ton of rock milled in 1911 was 20 pounds, compared with 20.5 pounds in 1910. The quantity of silver recovered was 497,281 fine ounces, an increase of 166,781 ounces over that of 1910. Of the silver, 513 ounces were obtained as pickings and 496,768 ounces were derived from the electrolytic treatment of 43,755,777 pounds of copper. The mines of Houghton County produced 83.9 per cent of the copper and 92.4 per cent of the silver output in 1911.

MAIZE PRODUCTS, AND MAIZE STARCH AND ITS PRODUCTS.*

The manufacture of starch and its products from maize, and the by-products which result therefrom, forms a large and actively growing industry in North America. A succinct general description of the processes by means of which the various proximate constituents of maize are separated from one another will perhaps be the best means of showing the characters of these products.

Steeping.—The dry grain from the granaries is conveyed into large hopper-bottomed steeping vats, and water impregnated with sulphur dioxide is run upon it. By means of steam syphons the water is kept in circulation and at the same time heated and maintained at temperatures varying from 120° F. to 140° F. This steeping process is continued for from two to four days, according as the corn is more or less amenable to the softening and disintegrating influences, or is required to be less or more friable or "soft" for the process to follow. The steep waters may be run to waste or may be evaporated for the recovery of the soluble material therein for the manufacture of cattle feed.

Milling.—The steeped corn is next run through Foos mills or their equivalent, by which means it is cracked, decorticated, and partially ground, giving rise to a diffuent mass. This, when appropriately diluted with water so that the most finely ground portions form a liquor (separator liquor), is passed through a germ separator—a long, large V-shaped tank with a screw conveyor at its bottom and skimming paddles at the top. The oil-bearing germ floats and is skimmed off, and the endosperm, starch and glutinous matter cortical tissues, bran, and fibre matter pass on.

The germ is then conveyed away, washed free from adherent starch and dried. The dried germ is next ground, "cooked" with live steam, and its oil expressed in hydraulic presses.

The resulting products are:

Corn oil, used largely in the manufacture of soap.
Oil cake, used as a cattle food. Composition:

Moisture	9.50
Protein	21.30
Fat	13.29
Carbohydrates	45.64
Fibre	8.27
Ash	2.00
	100.00

The cortical and endospermial portions, the most finely ground of which when suspended in water gives rise, as already stated, to the "separator liquor," are next screened by passing them over a vibrating copper sieve. The coarse material separated is lead into burr-stone mills, with the necessary quantity of water, and is finely ground, the effluent from the burr-stones being combined with the previously separated "separator liquor." This mixture is then pumped over the

*From Journal Society of Chemical Industry.

shakers. The first shakers are vibrating screens covered with silk bolting cloth of rather coarse mesh. By this means the starch "liquor" is separated from the wet "feed" or branny portions of the grain. This latter is conveyed into a stirring tub, agitated with water, and pumped over the second shakers, on which it is washed as free from starch as possible.

The bran is next conveyed to presses where water is squeezed out of it, and it emanates therefrom as "press feed," an article much used in that state as a cattle feed. Or after being dried in appropriate apparatus it is bagged and sold as "Corn Bran," the composition of which is:

Moisture	8.93
Protein	10.50
Fat	2.75
Carbohydrates	65.04
Fibre (insoluble).....	12.30
Ash	0.48
	100.00

The liquors separated from the shakers and mill are now combined and are known as the "Mill Liquor," or "Crude Starch Liquor." They may be passed over another series of fine sieves or shakers to screen out the more or less gritty, glutinous and fibrous residues, or they may be passed immediately over the runs, trays, tables, or gutters, these terms being used synonymously.

The runs are gutters about 120 ft. long, 6 or 8 ins. deep, and may be from 10 in. to 2 ft. wide, and above all, level, except for a drop of about 4 ins. between the ends. Into these the crude starch liquor is run and during its passage through them the starch, more or less free from gluten and cellular matter, is deposited, the glutinous and other residues "tailing off," carrying from 40 to 50 per cent of starch, which, however, cannot be economically recovered as starch. The run tailings are conducted into "continuous settling tanks," where the solids are allowed to subside, while the clear supernatant liquid is syphoned off and run into the sewer.

The run tailings so concentrated are sold as a liquid feed under the name of "Slop" or "Swill," or may be pumped through filter presses, the solid material collected, dried, and sold as gluten meal, the average composition of which is:

Moisture	9.74
Protein	31.20
Fat	2.35
Carbohydrates	54.67
Insoluble fibre.....	1.44
Ash	0.60
	100.00

This gluten meal is often mixed with certain proportions of corn bran while both are yet wet, the mixture dried and sold as "Gluten Feed," the average composition being:

Moisture	5.78
Protein	22.80
Fat	1.99
Carbohydrates	62.10
Insoluble fibre.....	6.68
Ash	0.65
	100.00

Those who have made comparisons of the dietetic values of protein-containing cattle feeds have found great advantages in using those feeds obtained as by-products of maize. Professor F. T. Shutt, of the Dominion Government Experimental Farm at Ottawa, considers that maize protein is the most efficient source of nitrogenous food for cattle, swine, etc.

The "green starch" which has been deposited on the "runs," containing about 50 per cent of moisture and about 0.5 per cent of protein, is now shoveled off and stirred up with water in the "breaker"; at this point it may be "converted" by acidulation and subjection to elevated temperatures under a pressure of about 30 lbs. per square inch for the necessary period of time. After conversion the resultant liquors are neutralized, filtered, clarified, or otherwise refined, after which they are concentrated into:

Glucose.—A highly refined, brilliant, thick syrup composed of water, dextrin, maltose and dextrose, and about 0.23 per cent of ash nitrogenous derivatives from protein; this is a very pure product and is a perfectly wholesome commodity, being quite as well refined as refined cane sugar. It appears on the market in concentrations varying between 43° and 45° B.

Grape Sugar.—A more fully converted product, with a higher "quotient of purity," i. e., with a greater percentage proportion of reducing carbohydrates (sugars) in relation to the total carbohydrates, and is consequently less dextrinous and more sugary than glucose. Unlike glucose it solidifies into a tough mass on cooling, which has a finely crystalline structure. The syrup for the production of grape sugar may be run into barrels while hot, where it is allowed to solidify, or it may be run into molds, allowed to solidify, and then chopped into lumps.

Corn syrup is an admixture of glucose with about 10 per cent of refined cane syrup and generally flavored artificially. It is a wholesome and delicious commodity especially adapted for use as a table syrup.

STARCH.

The "green starch" instead of being utilized for the production of saccharine products, may be manufactured into different varieties of starch to meet the various industrial and domestic requirements. This "green starch" may be passed over the "runs" a second time, the effect being that its gluten content is lowered from about 0.5 per cent to 0.3 per cent, and according to the use for which it is destined, it may or may not receive a "chemical" or "alkali" treatment with caustic soda before re-running.

The varieties of maize starch which are found in Canada on the market, may be classified as: (1) Thick boiling starches, (a) "Chemicalled," (b) "Unchemicalled," (2) Thin boiling starches—prepared by (a) the "drying-in-process," (b) the "in-suspension" process.

"Chemicalled" Starches.—The effect of alkali, as used in "chemicalling" starches, is to cause swelling

and flocculation of the protein and fibrous, and saponification of the fatty impurities retained by the starch, and to induce these to "tail off" and leave a purer and whiter starch when deposited a second time on the runs.

After passing over the runs, the starch, whether alkali or not, is shoveled into "breakers," suspended in water to form a liquor of a gravity of about 22° B., and then pumped into cloth-lined perforated boxes—the molding boxes—which are placed on the "boxing horses." By this means the water drains through the cloths, while the starch remains behind, and is subsequently "broke out" into large cubes of 7 to 8 in. edge. At this stage the starch contains 44-45 per cent of water. These cubes, after being broken out, are sometimes placed on porous bricks for a short time, water being abstracted from them and causing them to "set," the starch then containing 42-43 per cent of water. They are then removed to "crust kilns" and heated, which causes them to "sweat" until a browning on the surface ensues, followed by the formation of a thin dry crust all over the cube to a depth of about 1/6 to 1/4 of an inch. The lumps are removed from the crusting kilns, the "crusts" scraped off, and the inner scraped portions, containing from 28-30 per cent of water, are dried slowly or quickly in large cubes wrapped in paper, or may be broken into much smaller and more or less regular sized lumps, so as to produce the various "crystals" and "lumps," which are sold as "domestic laundry starches." When the starch is to be dried quickly it is broken up quite finely before being placed in the kilns, and when dry it is pulverized by grinding and then bolted. It is also put up as a ground or culinary starch; this is less alkaline than the laundry starches, having received a lighter caustic treatment, and better washing with fresh water after it has been treated, the result being a very highly purified commodity.

"Unchemicalled" starch may be dried as such more or less slowly and may be ground or not. It is used in the manufacture of baking powder or as a size in the textile industries. It is also used to a small extent by steam laundries.

All the foregoing starches are thick-boiling; that is, when cooked with boiling water they give rise to very viscous pastes which on cooling form somewhat stiff "jellies" which break with a glassy fracture.

Up to this point the manufacture of starch is a relatively simple matter, and the material which results very closely resembles in its properties the starch as it originally existed in the raw grain. On account, however, of the heating and action upon it of water, and of the sulphurous acid during steeping, and the alkaline treatments during its further purification, the viscosities of pastes produced from these starches are slightly less than that of starch obtained from the grain which has not been subjected to these influences. Again, the viscosity of unchemicalled starch is greater than that of chemicalled starch, and that of the scrapings from crusted lumps of chemicalled starch some-

what less than that of the inner portions of the lump.

The other starches which may be mentioned are those forming the so-called "thin boiling" or "modified" group. These starches, under so-called "standard" conditions and methods for testing, which are arbitrarily chosen by different workers, give rise, on boiling with water, or solution in a caustic alkali solution, to pastes of very much lower viscosities than thick boiling starches. Hence the name. They may be divided into two subdivisions according to the method of their manufacture.

1. The drying-in process.—Unchemicalled starch is suspended in water to about 22° B. and a certain quantity of hydrochloric acid is added to the "milk." It is then "boxed" and allowed to drain, the starch—containing 42-43 per cent of moisture and a small proportion of acid—is broken up and dried; during the drying process, starch, causing its viscosity to become less, but in little or no way altering the natural configuration of the starch granules unless temperatures high enough to cause their thorough dextrinization have been used, or unless they have been heated in the presence of moisture to temperatures above their swelling or gelatinizing points—65°-75° C. (149°-167° F.)

2. The in-suspension process.—Starch is suspended in water substantially as above, and a certain quantity of sulphuric or hydrochloric acid added. The mass is kept constantly stirred and is maintained at a temperature well below the gelatinizing point of starch but yet high enough to accelerate the hydrolytic action of the acid on the starch to a reasonable degree, and so to cause a diminution of the viscosity in direct proportion to the length of time, degree of temperature, and strength of acid, to which the starch is subjected. By inspection, even by means of the microscope, modified or thin-boiling starch cannot be discriminated from unmodified or thick-boiling starch.

These modified or thin-boiling starches are so manufactured as to give rise on boiling with water, to pastes of greater or less viscosity according to their application, which is for the laundry and confectionery trades.

The Laundry.—Before the introduction of thin-boiling starches and modern machinery, the ordinary thick-boiling starches were used in much the same way as they are in private households today. However, it was found that in order to cope with the ever increasing volume of work, especially the laundering of shirts, collars, cuffs, and those articles of apparel which demand stiffening, at a reasonable cost, and with expedition, changes had to be made in methods and materials. By a process of evolution mechanical devices for starching the goods were invented and improved, and in order to keep abreast with these contrivances, which are fundamentally used for driving large quantities of starch pastes into and between the folds of the materials to be starched, the starch makers had to alter the boiling properties of the starch supplied to laundries.

Starches from maize, rice, and wheat were used jointly or severally, and various combinations were essayed with more or less satisfactory results. The manufacture of maize starch has now been developed to such advantage as to completely replace rice starch, and almost completely replace wheat starch in the laundry trade in North America.

Thick-boiling, i. e., unmanipulated starches from these sources possess some distinctive physical characteristics. Maize starch gives rise to the most viscous pastes, less so wheat, and lastly, rice starch gives the least viscous paste. Hot maize starch pastes tend to revert relatively very slowly, wheat more quickly, and rice starch pastes most quickly. By reversion, I mean the separation of starch substances from their hot pastes on cooling. Again unmodified or thick-boiling maize starch pastes when applied to fabrics to be stiffened, cause them to become very stiff, board-like, and brittle, with but little pliability, while unmodified or thick boiling wheat and rice starch pastes stiffen very much less, but give rise to more pliable work; and in order that their work might possess both stiffness and pliability in a marked degree, and this is their great desire, laundrymen have used various combinations of maize and wheat starches, more or less thin boiling in character, or they have even used mixtures of thick and thin boiling starches to produce the desired results. I have known instances of three or even four different grades and combinations of thick and thin-boiling wheat and corn starches having been used. Complication and complexity in any industry is universally admitted to be a most undesirable feature, and the starch room of a laundry is no exception to this rule, so it is not surprising that efforts were turned towards the solution of the laundryman's starch problem.

Today, thin-boiling starches are being manufactured from maize starch which are capable of yielding the desired results in the laundry—pliable stiff work of good body which will not crack on being sharply bent. These results are obtained at smaller cost, and without the worries incidental to blending three or four starches, and probably making mistakes by taking two quantities from the same barrel, or omitting some of the ingredients, or both.

While this type of commodity, prepared from maize starch, has been on the market several years, its lack of uniformity in viscosity militated greatly against its general acceptance by the laundry trade, for which uniformity of starch is a vital point. Starch is applied to the goods after they have been washed, and the degree of stiffness in these starched goods is definitely elicited only after drying and ironing. If, after these operations, adding their quota of expense, the goods are not up to the standard, they have to be washed again, through every step, so as to rid them of their "old" starch and render them capable of absorbing starch anew. With every alteration in the viscosity of a starch supplied to a launderer, he must of necessity alter the proportions in which he uses it

so as to get his standard result. This keeps him in a constant state of uncertainty, for any hitch in his routine means more work and loss of money; an undesirable combination. Supply him with a starch of uniform viscosity, and his work is greatly facilitated and its quality ensured. The manufacture and the absolute control of viscosity of such a product has been accomplished for some time, and its introduction to the laundry trade has been attended with results gratifying both the manufacturers and consumers.

While fully 90 per cent of the steam laundrymen use a modified or thin boiling maize starch of the type portrayed, unmixed with any other starch, a proportion of them still clings to mixtures of thin boiling corn or wheat starches. As a general rule they use mixtures containing greater proportions of wheat than corn in the winter, when starched goods are required to be more pliable than stiff, while, for the converse reason more corn is used than wheat in the summer.

Many manufacturers prepare several starches of varying viscosity to suit the "needs"—I consider them whims—of their various clients; we have found it possible to supply the users of most diverse types of machinery and laundry methods with an absolutely satisfactory starch from one of two degrees of modification, a "Standard" and a "Special." Fully 95 per cent of them are supplied with the "Standard" viscosity. This very desirable state of affairs has been brought about by studying conditions in all sorts and conditions of laundries, and by manufacturing a grade of starch of such plasticity, which when made into a paste of a certain concentration determined by the requirements of the launderer, while somewhat "thick" or viscous, will yet penetrate into the goods and between its plies, and in which it will remain despite the "rubbing off" process to which they are subjected, before going to the drying room.

To convey some idea of the influence of viscosity and concentration on the character of laundry work, the following results obtained from some small batches of new cuffs which had not been previously laundered (i. e. they contained the original sizing material) will be interesting.

One hundred and forty-four cuffs were used for each experiment. The starching paste was made up at a concentration of 13.3 oz. of starch in the "cooked" gallon of paste. The air-dried cuffs were weighed before starching, and again after starching subsequently to being iron, and being allowed to stand over night.

	Weight per pair of cuffs. Before starch- ing, oz.	After starch- ing, oz.	Increase of weight due to starch, oz.	Character of work.
1. "Thin thin"....	1.26	1.36	0.10	Good pliability, fair stiffness and body.
2 "Medium thin"...	1.26	1.46	0.20	Good body, plia- bility and stiffness.
3. "Thick thin"....	1.26	1.41	0.15	Good body and stiffness, poor plia- bility.

Both thick boiling maize and potato starches are used in textile industries, but to the best of my knowledge no thin boiling starches are used in Canada in these industries.

Confectionery—Pulverized or ground starch is used in very large quantities for molding creams for chocolates, marshmallows, jelly beans, jujubes, gum drops and many other varieties of sweet-meats. The function of this molding starch is purely physical and mechanical. It is filled into trays, placed under the mold dies, which are embedded in it, and on their withdrawal they leave their impressions (molds). Into these the various kinds of confectionery are run while hot and more or less limpid, and on cooling they "set" and are conveyed and stacked in the drying rooms—large steam heated kilns—in which they are left for varying periods up to a week, to dry.

On completion of the drying process the trays and their contents are removed, allowed to cool and then are passed through a machine which separates the starch from the confectionery, brushes them free from starch, and packs the starch afresh into trays. With constant use, this molding starch becomes "dead," i. e., heavy and "wet" to the touch, compacts easily, and adheres to the moldies so that sharp imprints are not obtained. The acquirement of these undesirable characteristics is not due to the retention of water by the starch, but to the gelatinization of the starch granules where they come in contact with the moist, hot, sugary pastes—at least before they set—into the starch mass, and to the breaking off and admixture of small particles of the pastes therein. The combination of these circumstances causes the starch to become cloggy and impairs its ability to conduct and so evaporate moisture throughout its mass.

The gelatinized granules have no specific function in this process; they have lost for all time the ability to transmit moisture through or upon their substance, and also, on account of the fact that they adhere to the other granules with which they come in contact and form concretions, considerably diminish the extent of opposed surfaces and to that extent depress capillarity.

Again, the granules becoming sugar-logged and sugar-coated, offer greater resistance to the capillary transmission of water. The following data support this theory:

	Moisture per cent.
Fresh ground starch as supplied for molding.....	12.00
Molding starch after having been in use.....	9.00
Varying from 6.5 to 10.3 per cent.	

Fresh molded starch contains no soluble or deducing carbohydrate matters, while in every sample of "dead" molding starch examined, and previously sifted through a 200 mesh bolting silk, I have found not only abundant evidence of reducing carbohydrates, but a faintly sweet taste. In a sample examined quantitatively, I found the material to contain 1.6 per cent of soluble carbohydrates, calculated as dextrose (after their inversion). The not-inverted aqueous solution

also gave rise to osozones on treatment with phenylhydrazine. No attempt was made to discriminate between that of maltose and dextrose.

It must not be thought that a given amount of starch can be used indefinitely for molding. A considerable quantity of it is lost during the molding, and it is replaced by admixture of fresh starch. In this way the circle above alluded to, is in a measure, but not by any means wholly, guarded against.

The only satisfactory solution of this problem is, to thoroughly wash and purify the "dead" molding starch, and then dry and grind it.

However, I do not believe that it would be financially advantageous to the confectioner to have this "dead" molding starch worked over by the starch manufacturers. A more profitable means of disposing of it would be, I think, to arrange for its sale to cotton mills, or with paste makers, and to replace it by fresh molding starch.

When making up a batch of fresh molding starch from new ground starch, its texture is found to be too "light" or "lively." The molds made therein lack stability or "body." To combat this, wheat flour is sometimes mixed with it, but the desired consistency is more often given by mixing in some of the dead starch. This latter is the better plan, for the presence of gluten in the wheat flour cannot but exaggerate the formation of concretions, etc., when brought in contact with the moist steaming-hot pastes.

Gum-drops, or jujubes, should be composed of sugar, glucose, and gum arabic. Gelatin is also used in some varieties. Then there are gum-drops that contain no gum, its place being taken by starch. There are enormous quantities of these sold, and when properly made they are a delicious and wholesome form of confectionery. Before the introduction of thin boiling starches into the confectionery trade the ordinary thick boiling starch was used. It was found that a little of this went a long way. The difficulties of "burning" the kettle and of boiling the batches "dry" enough for dropping into the molds were great, and the resulting product was not invariably uniform. These difficulties were engendered by the thick, heavy, and to use the gum drop boilers term, "livery nature" of the starch. Then the thick boiling starches were used in conjunction with citric or tartaric acid. These ingredients were used to "cut" the starch and thin it down. The melange being of a more limpid consistency it is possible to boil it without "burning" and to get more water out of it in a given time, and so to "dry" it out to better advantage for dropping and for drying out in the drying rooms. However, more or less frequently sticky goods resulted which were of poor "body" and would not "stand up." The apportionment of acid and the regulation of its hydrolytic action on the starch could not be regulated definitely under the conditions existing in the kettles. Then came the thin boiling starches—starches "thinned down" on the same principles as the laundry starches,

but to which no "blue" had been added, so as to yield a type of confectionery with a sufficient body, but yet resilient and not tough, and withal, "smooth to the taste." This type of starch has found great favor with the confectioner, as with the launderer. It has solved the problem by enabling him to manufacture his desired product with speed and certainty, and has eliminated the necessity of using citric or tartaric acid. The ingredients as apportioned for making gum drops vary between very narrow limits, the variation being chiefly amongst the apportionment of sugar and glucose, accordingly as he requires a sweet, and slightly more expensive, or a not so sweet, and less expensive, product.

The percentage of starch in each variety of the commodity is practically constant. Water is merely added to allow of the thorough cooking and incorporation of the other ingredients, and it is evaporated during the boiling and drying of the batch. The function of the starch is, as we have said before, primarily to yield a material of a certain "body" and "texture." This desideratum is contingent upon two circumstances: the viscosity of the starch used, the proportion of the starch used, and as a corollary to these, the amount of water which the finished product can retain, without becoming sticky on the one hand, or tough and rubbery on the other. The percentage amount of starchy ingredient remaining the same, however, the characteristics evidenced during their manufacture while being boiled is, as would be expected, in direct relation to the viscosity of the starch used. The higher the viscosity, the more sluggish is the turn-over of the boiling mass in the kettle, and the longer does it take to boil the batch sufficiently dry for molding. Again, the palpable consistency and texture of the kiln-dried gum drops bears the same relation to the viscosity of the starch used in its manufacture; the higher the viscosity of the starch, the more tough and rubbery is the product, and capable of retaining its shape on pressure, and of returning to it when the pressure is relieved. However, the lower the viscosity of the starch used, the more "unctuous" and smooth to the taste is the resulting gum-drop. The amount of moisture retained by this kind of confectionery, after being withdrawn from the drying kilns, just previous to sugaring, is practically constant and varies between 18.5-19.0 per cent, except in the cases of starches of very low viscosity, giving rise to almost watery pastes, which retain about 12-14 per cent of water after drying. It was also observed that in air-dried and kiln-dried commodities from the same batch, the moisture contents at this period closely approximate one another, being respectively 20.5 per cent and 19.0 per cent. However, there is this difference in their consistency. Those that were air-dried when packed together tended to stick, while those that were kiln-dried exhibited no such disposition, with the exception of those made with the thinnest boiling starch, which were somewhat sticky, but in the opinion of others as well as myself, much more tasty and delicious.

On examining further into the matter of the air-dried and kiln-dried products, this fact was very evident. Those that were air-dried were practically of the same consistency throughout their mass, while those dried in the kilns, showed a well defined and desiccated "skin" on the peripheral portions, which were dried in contact with the starch at kiln temperatures. The bases of the gum-drops which are uppermost in the molding trays, and are exposed to the air, and not in contact with the starch, show "skinning" to a much less extent than the portions which were contiguous to the starch, so it is apparent that there is an accentuated drying influence brought about in this confectionery by its contact with starch at kiln temperatures.

Another very widespread application is in the poster-sticking industry, and also for sticking labels. Starch finds its way into leather goods, not as starch but as its hydrolytic product grape sugar which is largely used in the tanning industry.

The financial results of the turpentine industry in the United Provinces of India are stated by the Forest Administration to be very encouraging. The profit for last year was \$28,000 as compared with \$13,000 for the previous year. The excellent results are due to the phenomenal rise in price, turpentine having reached \$1.07 per gallon in March, 1911, at Calcutta, and rosin at \$2.31 per maund of 82 2-7 pounds, delivered at Cawnpore. The sale of the entire output of rosin for the year ended March 31, 1912, is assured at good prices, one lot of 25,000 gallons of turpentine being sold at 81 cents per gallon, delivered at Kathgodam. The same purchaser is to take the whole output of turpentine up to March 31, 1914, at rates based on current London prices for best American oil. Arrangements are being made to considerably extend this industry. All the chir forests of the division have been brought under revised tapping scheme on a 15-year rotation whereby from next year onward 250,000 trees will be tapped every year. In the Almora and Naini Tal district protected forests, a commencement has also been made with about 35,000 trees which are now under tapping. This operation will be extended in these forests, the possibilities of which are enormous.

According to J. P. Dunlop, of the United State Geological Survey, no galena concentrates were shipped to the smelters from the fluorspar mines in Kentucky in 1911, and in consequence no production of lead and silver was reported. The production of zinc carbonate concentrates in the state amounted to 467 tons, valued at \$10,604. The average zinc assay was 40 per cent, and the recoverable spelter content of the concentrates was 158 tons. As only 30 tons of zinc concentrates were shipped in 1910, the 1911 shipments show a substantial increase.

THE CHEMICAL ENGINEER IN THE PACKING HOUSE INDUSTRY.

By A. LOWENSTEIN.*

Science has been well defined as an *organized* knowledge of natural uniformities. In applying science to any industry then, the degree of success attained will be proportional to the ability of the scientist in organizing his knowledge of the various operations employed in an orderly manner, so that this knowledge can be promptly and efficiently applied to any particular problem, which may arise or be presented for solution.

In the evolution of the slaughter house of the early days into the packing house industry of today, with its various ramifications, utilizing its many by-products, the science of chemistry and the art of engineering have played an important part. At first the chemist was simply an analyst, making various analytical determinations on which valuations of various products were based and also for the information of the operating departments, to prevent waste.

Somewhat later, the scope of his analytical work increased so as to include analyses of various purchased products and the working out of methods of analyses for the better detection of adulteration of these products and specifications for their purchase. During this early period it gradually became recognized that a chemist was frequently a good man to have out in the "plant" and that not all chemists were "theoretical" as was at one time commonly supposed, and that they could do things occasionally which had practical value. This was about the time that a new species was being born in other industries, a sort of a hybrid, if you please, the "Chemical Engineer" who is rapidly taking his place in all industries. All of the leading universities during the past five years, have or are now establishing courses in chemical engineering.

To make the matter more concrete, what are some of the subjects which a chemical engineer in a packing house should know?

First—He should be thoroughly conversant with the principles of evaporation, drying and distillation, under atmospheric conditions and also under vacuum and pressure.

In the case of driers, he should be able to utilize this knowledge in the selection of machinery and to obtain the highest efficiency from it after it is selected. Many different types of driers are employed in packing houses, for the handling of fertilizers, bones, glue, etc.

He should be familiar with different types of vacuum evaporators, for the evaporation of tank water, glue, beef extract and similar products and with many other types of vacuum machinery em-

ployed in oil refining, canning of meats, beef extract products, ammonia, etc.

If the packing house manufactures ammonia products, he must be familiar with various distilling processes and different types of stills. In the same connection he should understand commercial methods of crystallization and fractional crystallization in the "seeding" of various fats and oils which are to be subsequently pressed for the partial separation of their harder constituents, commonly known as "Stearine."

He should be familiar with the different types of presses used for this purpose, viz., knuckle joint, weight, hydraulic and screw presses, both of the intermittent and continuous types.

He should be familiar with the operation of different types of filters, both gravity filters and filter presses, steam and motor driven pumps, for hot and for cold liquids, with various types of conveyors, tanks, retorts, butter churns and workers employed in making oleomargarine and dairy products, etc., etc.

He should be conversant with the various kinds of materials of construction, their inspection and the testing thereof. This applies to Portland cements, brick, steel for reinforced concrete, asphalt for floors, insulating materials for coolers and refrigerator cars, steel for tanks, car wheels and journals, galvanized iron, etc., etc. The proper selection of the correct material of construction for a definite piece of work is of the greatest importance. He should keep posted on the progress made to prevent corrosion of iron and steel and coated metals such as tin plate and galvanized iron and steel. In this connection he must inspect and analyze paints and varnishes. This is a matter of great importance inasmuch as many paints on the market are themselves accelerators of corrosion.

He should be familiar with different kinds of fuel, solid, liquid and gaseous, as all three are employed at one point or another at the different packing centers.

He should be familiar with boiler practice and the means of securing the most complete and efficient combustion of the fuel. He should make frequent gas analyses of flue gases to determine this. He must be familiar with lubrication in order to select the most suitable oil for various kinds of machinery employed.

He should be thoroughly posted on water purification, both for industrial and potable purposes. When a new packing house is started there is no point of greater importance than the water supply. Questions are at once asked: What effect will the water have on meats, on oleo oil, lard, tallow and glue, in the boilers, etc.? The water situation at each of the different packing centers varies greatly and requires considerable study.

He is frequently called on to make sanitary and bacteriological examinations of water and of ice used in contact with edible products.

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He is required to understand and operate air purifying apparatus, both used in agitating and purifying edible oils and fats. In connection with the handling of various fats and oils, he should be familiar with refining by means of chemicals; with bleaching, both by physical means, such as with fuller's earth and by chemical agents and with various deodorizing processes.

In connection with fertilizers, he should understand the manufacture of sulphuric acid, acid phosphate, mixed fertilizers, etc.

In connection with the curing of meats, he should understand the various properties of solutions of varying concentration and solution pressure and the influence of temperature. Lack of definite knowledge on this subject results in very great losses of money annually to many packers, who either waste money by using too much saltpetre, sugar and salt or through loss of meat, because their solutions or temperatures were not properly adjusted. At this point it might be stated that in the last few years it is being recognized that a bacteriologist and physiological chemist can be of great value in determining causes of improper curing and to develop means for remedying such difficulties.

A bacteriologist in a packing house can also be of much value in connection with various dairy processes usually carried on in a packing house in connection with milk for oleomargarine, renovated butter, etc., and in many other ways.

It is of advantage for the chemical engineer in a packing house to attend meetings of scientific societies and trade organizations and to keep thoroughly abreast of the times by regularly reading many scientific and trade journals, both of his own and allied professions and industries.

In the chemical laboratory of the modern packing house, which is usually organized into divisions, for the sake of simplicity, the large variety of the manufactured products of the packing house regularly are analyzed. All supplies purchased are sampled, inspected and tested. Invoices for these supplies, in most cases, have to be approved by the laboratory prior to payment. A research laboratory is maintained where trained men are always at work endeavoring to solve the difficult problems of the industry and to apply the results of their labors. When a new process is devised, it is tried out first on a small scale in the laboratory until its merits are demonstrated and then in the factory first on a small scale and then, if successful, on a gradually increasing conservative scale.

It is apparent from the above that the packing house chemical engineer in order to be successful, should always be a student, always ready to listen to suggestions from others, to co-operate with all departments, to adopt successful processes from other industries and to be able to initiate and develop new methods and processes commercially.

ALUMINUM PRODUCTION IN 1911.

Aluminum, comparatively few years ago a rare metal, too expensive to have any particular economic value, has today come into wide use in a great number of industries. The consumption in the United States in 1911, according to the U. S. Geological Survey, was 46,125,000 lbs., the price in New York ranging from 18½ to 22 cts. a pound. The Survey has just published a report by W. C. Phalen on "Bauxite and Aluminum," an advance chapter from "Mineral Resources of the United States" for 1911, which gives a comprehensive review of the industry for the year. Bauxite ore, the present source for metallic aluminum, is mined in Arkansas, Georgia, Alabama and Tennessee, the output from these states combined amounting in 1911 to 155,618 long tons, valued at \$750,649, an increase of about 5 per cent in both quantity and value compared with the figures for 1910. The increase, though small, shows a healthful condition of the industries dependent on this ore for raw material. The chief uses of bauxite are in the manufacture of metallic aluminum, of aluminum salts, of alundum or fused alumina, which finds extensive use as an abrasive, and to a minor extent in the making of bauxite brick and of plaster compositions. The first three industries mentioned consume the bulk of the ore now mined. In the aluminum industry a new plant located at Clarksburg, West Virginia, is reported to have begun operations in January, 1912, having for its object the manufacture of metallic aluminum and its compounds. The use of the metal aluminum and its alloys in automobiles, dirigible balloons, and aeroplanes is constantly increasing. In the form of magnalium it is used in the beams of analytical balances, and other new alloys are being constantly brought to public attention. The metal is also employed in paper decorations and for wrapping. It is reported to have been used in the textile industries, where it has been combined with silk, to which it imparts a peculiar brilliancy, particularly adapted to theatrical and ceremonial costumes. It has found and is constantly finding a host of applications in smaller articles of everyday use and ornamentation. The Ordnance Department of the United States Army recently awarded a contract for sixty thousand or more aluminum canteens and cups. The metal is now being used in various other ways in the light field equipment of the army.

The report contains statistics of production, consumption, and world's production of bauxite; production and imports of aluminum salts; and consumption and exports of metallic aluminum. Descriptions are given of the occurrence and possible new sources of aluminum salts in Utah and Alabama, the bauxite fields in the southern state, the uses and methods of purifying the raw ore, the manufacture of aluminum, and the aluminum market conditions for the year. The alloys of aluminum, an attractive field of research, are also discussed.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

II.

Iron Ore Analysis.—The substances usually determined are the following: Iron, silica, sulphur, phosphorus and manganese. Determinations of lime and magnesia are occasionally called for. All determinations are made upon the air-dried sample.

The Determination of Iron.—Iron is determined by titration with potassium permanganate in the presence of hydrochloric acid. This method is very convenient, and by the observation of a few precautions may be made accurate.

Preparation and Standardization of Permanganate Solution.—The permanganate solution of a strength of about 2.9 gms. of the crystallized salt per litre should be made up some weeks in advance of standardization to insure complete oxidation of organic water, and before use, should be filtered through asbestos to remove all traces of MnO_2 . This solution will have a standard of 1 cc. = 0.005 gms. iron, approximately.

Iron wire of known purity and standard iron ore are used for standardization.

The procedure in the former case is as follows:

Samples of wire of 0.2 gm. each are weighed into Erlenmeyer flasks (250 cc.) and boiled with 10 cc. of HCl (1:2). The flask is removed from the hot plate when solution is complete and reduced by the addition, drop by drop, of a 20 per cent $SuCl_2$ solution until colorless. The reduced solution is poured into a beaker containing 25 cc. of a saturated solution of $HgCl_2$, the flask rinsed, the whole diluted to 300-350 cc. with cold water, 25 cc. of "preventive solution" added and the solution titrated very slowly (so slowly that the drops might be counted) and with constant stirring until the pink color persists for about a minute. Duplicate samples should check mostly.

Wt. of wire $\times$ % Fe

———— = Fe st'd.

cc.

Fe St'd

———— = factor.

.005

The standard by the above method checks very closely the standard determined upon iron in the presence of H_2SO_4 , and that from pure oxalic acid.

When standard iron ore is used the procedure is

exactly that used in the treatment of the unknown sample.

The Determination.—Half gram samples are treated in Erlenmeyer flasks with 5 cc. $SuCl_2$ solution and 10 cc. strong HCl and digested until the residue is white. The partially oxidized solutions are then removed from the flame, reduced by $SuCl_2$ solution added dropwise, poured into $HgCl_2$, "preventive solution" added, and the titration carried on exactly as in standardizing.

The special precautions necessary are the following: The minimum quantity of HCl should be used, reduction should be accomplished with the least possible excess of $SuCl_2$ to keep the bulk of precipitate of $HgCl_2$ small, and the titration should be made slowly in cold solution—cc. $KMO_4 \times$ factor = % Fe.

If the residue after treatment with HCl and $SuCl_2$ remains dark and so is suspected of containing iron, as in the case of ores containing magnetite, the residue is filtered, fused with 2 to 3 gms. of $KHSO_4$ until decomposed, the melt extracted with water and HCl, the iron reduced and titrated as above. The quantity found is added to the percentage of soluble iron.

Determination of Silica.—The sample (1 gm.) is treated with 20 cc. conc. HCl in a small casserole and boiled gently to complete decomposition and then evaporated to dryness on the water bath and baked for an hour at $120^\circ C$. The dry residue is thoroughly moistened with strong HCl, taken up with hot water, and the whole boiled, filtered, washed, burned and ignited in an unweighed platinum crucible. To the thoroughly ignited residue, a drop of H_2SO_4 and 2 to 3 cc. of HF are added, the whole evaporated dry, the residue again blasted, and the crucible and residue reweighed. The loss in weight represents the SiO_2 , volatilized as SiF_4 .

The methods to be described for the determination of sulphur phosphorus and manganese are directly applicable to ores which may be completely decomposed by acids. For more refractory ores, modifications will be given.

Sulphur.—The 2.5 or 5-gm. sample is heated on the hot plate to complete decomposition with 20 to 40 cc. strong HCl and 5 to 10 cc. HNO_3 , and evaporated to dryness, without baking. The residue is taken up in 25 cc. HCl (conc.) and evaporated to the appearance of solid $FeCl_3$, a little HCl added to make solution complete, and the whole diluted to 75 cc., filtered and the residue washed free from iron. To the filtrate, $BaCl_2$ solution (5 cc. 10% $BaCl_2$), is added the whole, again evaporated to the first separation of solid ferric chloride, a few drops of HCl added and the solution

*90 gms. $MnSO_4 \cdot 7H_2O$, 650 cc. H_2O , 175 cc. conc. H_2SO_4 and 175 cc. H_3PO_4 sp. gr. 1.75.

diluted to 200 cc. with cold water. After standing some hours (preferably over night), the BoSO_4 is filtered off, ignited and weighed.

Wt. $\text{BoSO}_4 \times 0.1374$

$$\frac{\text{Wt. sample.}}{\text{Wt. sample.}} \times 100 = \% \text{ S.}$$

If the residue is suspected of containing sulphur it is ignited in a platinum crucible and fused with five times its weight of Na_2CO_3 plus a small crystal of KNO_3 . The melt is taken up with water and HCl , the solution filtered and BaCl_2 added, care being taken to keep down the excess of HCl . The resulting weight of BoSO_4 is added to that obtained from the soluble portion of the ore.

In general, fusions for sulphur should be made over an alcohol blast lamp, or in an electrically heated muffle, in a room free from fumes of SO_3 . If a gas flame is used a "blank" should be run and the weight of BoSO_4 obtained in it deducted from that formed in the determination.

Phosphorus.—The acid-alkali titration of the precipitate of ammonium phospho molybdate is the method used.

Solutions of NaOH and HNO_3 of about tenth normal ($\text{N}/10$) strength are prepared and their ratio determined, using phenol phthalein as indicator. They may be standardized in several ways. The best is to employ a standard iron ore, of known phosphorus content, treating it exactly as the unknown ore is treated. Failing this, the following method gives excellent results: A solution containing about 0.1 gm. of Ma_2HPO_4 is treated with 5 cc. NH_4OH , 10 of HNO_3 and 100 cc. ammonium molybdate solution (3%), the whole heated to 80° and shaken for five minutes. The resulting precipitate of ammonium phospho-molybdate is allowed to settle, filtered on a hardened paper, washed with 1% HNO_3 and then twice with alcohol and dried at 110° . This precipitate contains 1.63% phosphorus. Samples of it of about 0.1 gm. each are weighed out into Erlenmeyer flasks, 40 cc. of the NaOH solution added, and the excess of NaOH titrated with the HNO_3 , phenol phthalein being used as before.

Wt. $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{NaO} \cdot \cdot \cdot \times .0163$

$$\frac{\text{Wt. sample.}}{\text{cc. NaOH.}} = \text{P. per cc. of}$$

NaOH.

Determination.—Samples of 2.5 gms. are decomposed by HCl and evaporated almost dry. HNO_3 is added in excess and the evaporation carried to the elimination of HCl . The nitric acid solution is evaporated dry, taken up with a little HNO_3 and hot water, and the residue of silica removed by filtration. The filtrate diluted to 100 cc. in a 400-cc. Erlenmeyer, is made first alkaline with NH_4OH , and then acid with HNO_3 and a 5 cc. excess of HNO_3 added, and the whole heated to 80°C. , 50 cc. of ammonium molybdate (3%) is then added, and the solution shaken vigorously

for 5 minutes. The precipitate is allowed to settle, and then filtered, washed free from iron with 1% HNO_3 solution and finally freed from acid (by test with methyl orange on a spot plate) with 1% KNO_3 . Precipitate and filter are transferred to flasks, 40 cc. of the standard NaOH run in, and the excess titrated, as in the standardization, with HNO_3 .

Cc. of NaOH used $\times \text{P std} \times 100$

$$\frac{\text{Wt. of sample}}{\text{Wt. of sample}} = \% \text{ P.}$$

Wt. of sample

When the ore is not completely decomposed by acids, the sample is fused with four times its weight of Na_2CO_3 in a large platinum crucible. The fusion is decomposed by HNO_3 and water and the solution evaporated to dryness and silica dehydrated. The residue is taken up with HNO_3 and water, the silica filtered off, and the filtrate made, first, alkaline with ammonia, then acid, plus a 5 cc. excess, with HNO_3 and the determination completed exactly as above.

To be successful, the above method for phosphorus demands a pretty close adherence to conditions throughout.

Manganese.—The Volhard volumetric method is used. For the small quantity of manganese usually met with in iron ores, the KMnO_4 used for the titration of the iron is too strong, so a portion of it should be diluted to exactly $1/5$ strength.

The method depends upon the oxidation of MnO (as MnSO_4) to MnO_2 in the presence of ZnSO_4 in solution made neutral by ZnO .

Since $2\text{KMnO}_4 = 10 \text{ Fe}$ and $2\text{KMnO}_4 = 3\text{Mn}$ (neutral solution), then $10 \text{ Fe} = 3 \text{ Mn}$ and $559:156:1$, the Fe Std. , the Mn Std.

A 2.5-gm. sample of ore is decomposed by 25 cc. HCl and evaporated to small bulk, when 5 cc. H_2SO_4 is added and the whole evaporated over the fire flame to copious fumes of SO_3 . The cooled mass is taken up with water and solid Na_2CO_3 added until the precipitate of $\text{Fe}(\text{OH})_3$ just redissolves.

The solution is transferred to a 250-cc. measured flask, and an excess of zinc oxide emulsion added (ZnO triurated with water to the consistency of cream), the flask filled to the mark with water and shaken. A portion of the solution is filtered through a dry filter (the first few cc. being discarded) into a 100-cc. measured flask, and the filtrate, to which a drop of the zinc acid emulsion is added, is transferred to a casserole, heated to boiling and titrated at boiling temperature and with vigorous stirring, with KMnO_4 until the first permanent pink color. The precipitate of MnO_2 formed should coagulate and settle readily, leaving a clean solution in which the first pink color may be detected against the white walls of the casserole.

It is best to determine the manganese standard directly against a standard iron ore containing about 0.5% Mn , using the method exactly as described for the determination in the unknown ore.

The 250 flask containing the solution contains a large bulk of $\text{Fe}(\text{OH})_3$ precipitate, as well as the excess of ZnO , so 100 cc. of clear solution represents more than $\frac{2}{5}$ of the total sample. If a direct determination of the standard is made, this error is eliminated. If the standard is calculated from the iron standard, a satisfactory correction may be made as follows: The sample is made up to 500 cc. and 100 cc. taken as before. The solution in the flask is again diluted to the mark and another 100 cc. taken and titrated. The average of these two titrations gives a corrected result which is very close to the true value.

cc. of $\text{KMnO}_4 \times \text{Mn Std}$

Wt. of sample

$\times 100 = \% \text{ Mn.}$

THE REFRACTIVE INDEX OF BEESWAX.*

By L. FELDSTEIN.†

Lewkowitsch, in Chemical Technology and Analysis of Oils, Fats and Waxes, recommends refractometric examination as a preliminary test in the examination of beeswax, giving as the limits between which pure beeswax should fall, 42.9° - 45.6° , butyro-refractometer scale, calculated to 40° C. These figures were obtained from the work of Werder¹ and Berg,² who made the determinations at temperatures ranging between 70° and 84° C. and then calculated them to 40° C. Neither Werder nor Berg in their original articles give the figures actually observed nor explain how their calculations were made, but it is assumed that they added to the observed figures the correction 0.55° butyro for each degree centigrade between the observed figures and 40° C. ; the correction value 0.55° being generally used for all fats and oils when calculated to 40° C. In this laboratory an Abbe-Zeiss direct-reading refractometer is used, and for beeswax a correction of 0.00037 per degree centigrade was found necessary. This figure was obtained by taking the refractive index at 65° , 75° , and 85° C. and dividing the difference in the reading by the difference in degrees centigrade. This correction of 0.00037 per degree centigrade was found to be practically constant between these temperature limits not only for all pure beeswax examined, but also for those which, upon further examination, showed adulteration.

As beeswax is a solid at 40° C. and the refractive index is always read on the melted wax at some temperature above 63° C. , it seems desirable to eliminate the use of the calculation to 40° C. and to set limits for the refractive index of pure beeswax at some temperature above the melting point. For this purpose a number of samples of known purity and origin, obtained from the Bureau of Entomology, United States Department of Agriculture, and some others purchased on the open market were examined. All

of these had been analyzed by the drug laboratory of the Bureau of Chemistry. The readings were made at 65° , 75° and 85° C. , and the results are given in the following tables. Table I consists of the figures obtained on the samples of pure beeswax secured from the Bureau of Entomology. Table II shows the results on those samples obtained in the open market, many of them adulterated samples. In the column headed "Remarks" are placed conclusions as to the nature of the sample based on the chemical analysis:

TABLE I.—REFRACTIVE INDEX READINGS AT DIFFERENT TEMPERATURES ON BEESWAX SAMPLES OF KNOWN PURITY.

Contract		Refractive index.			Locality.
laboratory No.	At 65° C.	At 75° C.	At 85° C.		
12616.....	1.4458	1.4424	1.4390		Not given.
12617.....	1.4458	1.4425	1.4391		"
12618.....	1.4456	1.4420	1.4380		"
12619.....	1.4454	1.4418	1.4378		"
12620.....	1.4449	1.4414	1.4380		Mexico.
12621.....	1.4453	1.4416	1.4377		N. Carolina.
12622.....	1.4460	1.4426	1.4388		Wisconsin.
12623.....	1.4441	1.4403	1.4365		Cuba.
12624.....	1.4449	1.4412	1.4375		Habana.
12625.....	1.4448	1.4410	1.4374		Haiti.
12626.....	1.4448	1.4414	1.4374		Southern states
12627.....	1.4458	1.4424	1.4387		Africa.
12628.....	1.4456	1.4420	1.4384		New York.
12629.....	1.4488	1.4451	1.4415		San Domingo.
12656.....	1.4440	1.4402	1.4363		Not given.
12657.....	1.4443	1.4406	1.4367		Wisconsin.
12658.....	1.4460	1.4424	1.4388		Illinois.
12659.....	1.4449	1.4413	1.4377		Texas.
12660.....	1.4444	1.4405	1.4368		Iowa.
12661.....	1.4450	1.4413	1.4378		Utah.
12662.....	1.4458	1.4422	1.4384		Iowa.
12663.....	1.4444	1.4405	1.4368		California.
12664.....	1.4436	1.4398	1.4361		Hilo.
12665.....	1.4434	1.4398	1.4361		"
12666.....	1.4435	1.4400	1.4362		"
12667.....	1.4447	1.4410	1.4375		Not given.
12801.....	1.4470	1.4433	1.4395		Minnesota.

TABLE II.—REFRACTIVE INDEX READINGS AT DIFFERENT TEMPERATURES ON COMMERCIAL SAMPLES.

Contract		Refractive index.			Remarks.
laboratory No.	At 65° C.	At 75° C.	At 85° C.		
12630.....	1.4463	1.4425	1.4389		Pure wax.
12631.....	1.4459	1.4425	1.4387		"
12632*.....	1.4379	1.4340	1.4302		Paraffin pres-
12633.....	1.4456	1.4421	1.4387		Pure wax. [ent
12634*.....	1.4380	1.4344	1.4307		Paraffin pres-
					ent.
12635*.....	1.4379	1.4342	1.4302		Stearic acid
					and paraffin
					present.
12636.....		1.4540	1.4505		Resin present.
12637*.....	1.4375	1.4338	1.4301		Paraffin pres-
12638*.....	1.4350	1.4313	1.4275		" [ent.
12639.....	1.4448	1.4410	1.4372		Pure wax.
12640.....	1.4454	1.4416	1.4380		"
12641*.....	1.4421	1.4384	1.4346		Paraffin pres-
12642*.....	1.4363	1.4323	1.4284		" [ent.
12643.....	1.4447	1.4410	1.4372		Pure wax.
12644.....	1.4437	1.4400	1.4364		"
12645.....	1.4440	1.4402	1.4368		"
12646.....	1.4445	1.4410	1.4372		"
12647.....	1.4438	1.4401	1.4362		"
12648*.....	1.4421	1.4384	1.4348		Paraffin pres-
					ent.
12649*.....	1.4335	1.4300	1.4260		Stearic acid
					and paraffin
					present.
12650*.....	1.4342	1.4304	1.4268		Paraffin pres-
12651.....	1.4439	1.4402	1.4365		" [ent.
12652*.....	1.4345	1.4307	1.4269		"
12653.....	1.4445	1.4408	1.4372		Pure wax.
12654*.....	1.4355	1.4318	1.4280		Paraffin pres-
					ent.
12655.....	1.4441	1.4406	1.4369		Pure wax.

*Grossly adulterated samples.

Upon examining the tables it will be found that the refractive index at 75° C. for pure beeswax falls be-

*U. S. Dept. Agr., Bureau of Chemistry, Cir. 86.

†Contracts Laboratory, U. S. Bureau of Chemistry.

tween 1.4398-1.4451. Table II shows that the refractive indices of all those samples bought in the open market, which on chemical analysis appeared to be pure, fell within the limits for pure beeswax (1.4398-1.4451); while of the adulterated samples only one fell within these limits. This sample was No. 12651, which has a refractive index of 1.4402, a figure very close to the lowest value obtained for pure beeswax. In this instance it is quite possible that the beeswax had a high refractive index and was adulterated with a small amount of paraffin. One sample (No. 12636), showing a high refractive index of 1.4540, proved on chemical examination to have resin in it. It was not possible to obtain a clear reading of this wax at 65° C. Those samples which have a very low refractive index proved to be grossly adulterated with either paraffin or stearic acid, or both. A temperature of 75° C. was selected because at this point all beeswaxes are liquid, a clear sharp line can be obtained in the refractometer, and it is comparatively easy to make the reading.

It is seen that the determination of the refractive index of beeswaxes is of great help in detecting gross adulteration and will generally reveal small adulterations, samples containing only a small amount of foreign material generally giving figures outside the limits mentioned, namely, 1.4398-1.4451 at 75° C. The results obtained show also that it is both unnecessary and unwise to calculate the refractive index to the butyro scale at 40° C., for the following reasons: (1) It is unreasonable to report the refractive index of a wax at a temperature at which it is an opaque solid, when the actual reading is made on the melted wax. (2) The calculation consumes time. (3) A clear reading can be obtained at 75° C. and the figures obtained can be reported unchanged.

The U. S. Consul at Bradford, England, reports that the Textile Institute recently held a conference in Bradford at the suggestion of some local manufacturers to consider the propriety of fixing a standard dye for textiles sold as "indigo dye" or "warranted indigo dye." At present goods so described, which some people believe contain no dye other than indigo, may contain as little as 1 per cent of indigo dye, and as there is now no definite standard in this country as to the amount or quality of indigo necessary to warrant the sale of cloth so described, the Textile Institute was asked to call together representative scientists, dyers, and manufacturers to consider the matter. It was decided at the Bradford meeting that before holding a combined meeting at Bradford the several sections of the textile industry should meet separately, the cotton section at Manchester, the linen industry at Belfast, and the woolen and worsted section at Bradford. This was deemed advisable owing to the difference existing between the different trades as to the degree of purity that would be acceptable in goods stamped as pure indigo dyed.

THE CAUSES FOR VARIATIONS IN VOLATILE MATTER DETERMINATIONS.*

By S. W. PARR.

While the method for the determination of volatile matter in coal must doubtless remain empirical in character, it is evident that concordant results can come only from a procedure which is based upon a knowledge of the relative influence of the various factors that enter into the process. It seems probable that essentially all of the variations may be referred to one or more of the following conditions:

- (a) Mechanical loss;
- (b) Oxidation under the cover;
- (c) Variation in the discharge of hydrogen in the latter part of the process;
- (d) The speed of decomposition in the early carbonization of the coal.

It is the purpose of this note to indicate that the variations under (a), (b) and (c) are small in amount and easily controlled or eliminated, and that practically all of the variation centers in (d) and depends upon the speed with which the heavier or richer volatile constituents are discharged from the mass.

(a) *Mechanical Loss*.—The difficulty of mechanical loss has already been discussed in a former paper.¹

Further experience in the use of a small amount of kerosene as therein recommended is confirmatory of the advantage of that procedure as a means for lessening the mechanical loss and promoting uniformity of results.

(b) *Oxidation Under the Cover*.—It seems evident that the ordinary flat cover to a platinum crucible, no matter how well fitting so far as the eye can determine, is nevertheless responsible for many irregularities, possibly due to slight displacement of the cover at the time of greatest evolution of gases. To guard against this difficulty, the suggestion of Shimer² has been used, namely, providing a small platinum capsule with rather light flexible sides which would fit into the main crucible and adjust itself to the irregularities of the same, thus providing a good fit without the overhanging feature of the flat cover with its tendency to promote air currents in and out of the crucible. That this device is a positive help towards uniformity is shown from the following table. The samples were given identical treatment as to heat and time. Fifteen drops of kerosene were used in both series to eliminate variables due to mechanical loss, the only difference being the use of an inserted capsule as a cover in one case, Series B, and a regular flat, well-fitting cover in the other, Series A:

TABLE I.—SUMMARY OF THIRTEEN RESULTS.

	A.	B.
Extreme of variation in duplicates.....	0.39%	0.21%
Number of duplicates having variations from the average less than 0.1 per cent.....	4	10
Average of total variations.....	0.16%	0.07%

*From the Journal of Industrial and Engineering Chemistry.

¹Journal Industrial and Engineering Chemistry.

²Ibid., 1, 518 (1909).

(c) *Residual Hydrogen*.—The extent to which the residual volatile matter, mainly hydrogen, is driven off, is a possible source of variation, but the variable is easy of control. A study of the work of Porter and Ovitz,³ and also of Burgess and Wheeler,⁴ shows that the discharge of hydrogen is quite uniform for a given temperature, and that with bituminous coal the volatile matter as represented by this element is given off much more rapidly below 900° than above that temperature; so that if a temperature above 900° is maintained within reasonable limits the variation in the indicated volatile matter will be small.

At temperatures of 1050° or 1100° the discharge of this constituent is so nearly complete that very close check results should be expected. At a temperature approximating 950° the results should still check with themselves, but the indicated volatile matter would be less than with the higher temperatures. The ratio of difference would doubtless vary slightly with different coals. The conditions thus indicated call for a uniform heat which may be maintained at a reasonably uniform temperature and above 900°. Whether it shall be arbitrarily placed near the lower limit, say, 950°, with an incomplete discharge of the volatile matter, or near the upper practicable limit, say, 1100°, with a more nearly complete discharge of volatile, it is not the purpose here to decide. It is desired now only to show how closely the above proposition is confirmed by the data at hand.

A number of coals were tested in duplicate under identical conditions as to (a) use of kerosene, and (b) capsule cover. The heat applied for Series A was 950° to 980° throughout, as obtained by use of a Méker burner. In Series B the same heat from the same burner was applied for two minutes. The crucible was then subjected for five minutes to a temperature of 1100°. They indicate that by eliminating all other variables, the completeness of the hydrogen discharge for a given temperature is very definite, increasing noticeably in exactness with the higher temperatures and the more complete discharge of the hydrogen. So far as these results go, at least, they furnish a striking verification of the above proposition concerning the hydrogen variable.

In order to determine whether lower temperature for the first two minutes of heating would be neutralized in its effect by the subsequent increase for five minutes to 1100°, a number of the coals in Table II were subjected to a much lower temperature, approximately 500° to 600°, or such that the time for driving off the heavy volatile material was noticeably prolonged, though still practically completed within the two minutes allowed in Table II. These results show that the lower temperatures cause a larger fixation of carbon and a consistently lower percentage of volatile matter, thus confirming the proposition as stated under

TABLE II.—COMPARISON OF DUPLICATES USING DIFFERENT TEMPERATURES FOR LAST PART OF PROCESS.

Lab. No.	Kind of coal.	7 min. at 950°. Per cent.	Variation + or — from average. Per cent.	2 min. at 950°. 5 min. at 1100°. Per cent.	Variation + or — from average. Per cent.
4513	Fulton Co.....	42.01 41.85		42.80 42.77	
4516	Sangamon Co...	41.93 39.70 39.73	0.08	42.78 40.71 40.70	0.02
4517	Sangamon Co....	39.71 39.60 40.03	0.02	40.70 41.10 41.06	0.01
4518	Sangamon Co....	39.81 37.37 37.33	0.22	41.08 38.91 38.88	0.02
4519	Sangamon Co....	37.35 38.81 38.78	0.02	38.90 40.16 40.19	0.02
4520	Sangamon Co....	38.80 40.09 40.37	0.02	40.18 41.13 41.10	0.02
4521	Sangamon Co....	40.23 39.61 39.82	0.14	41.12 40.98 41.02	0.02
4522	Sangamon Co....	39.71 40.31 40.27	0.11	41.00 41.44 41.44	0.02
4523	Logan Co.....	40.29 40.41 40.36	0.02	41.44 40.94 40.91	0.00
4524	Logan Co.....	40.38 39.27 38.98	0.03	40.93 40.21 40.21	0.02
	Average of variations.....	39.12	0.15	40.21	0.00
			0.08		0.015

TABLE III.—SHOWING THE EFFECT ON VOLATILE MATTER OF DIFFERENT TEMPERATURES FOR THE FIRST TWO MINUTES OF HEATING.

Lab. No.	Kind of coal.	2 min. at 950°. 5 min. at 1100°. Per cent.	2 min. at 600°. 5 min. at 1100°. Per cent.	Difference in average values.
4519	Sangamon Co., Ill.....	40.16 40.19	38.91 38.86	
4520	Sangamon Co., Ill.....	40.18 41.13 41.10	38.89 39.45 39.77	—1.29
4521	Sangamon Co., Ill.....	41.12 40.98 41.02	39.61 35.59 39.69	—1.51
4522	Sangamon Co., Ill.....	41.00 41.44 41.44	39.64 40.10 39.97	—1.36
4523	Logan Co., Ill.....	41.44 40.94 40.91	40.03 40.01 40.03	—1.41
	Average	40.93	40.02	—0.91 —1.30

(d) as to variations caused by the speed of the preliminary decomposition. Also by the close agreement of the duplicates there is added further confirmation to the proposition under (c) as to the constancy of the hydrogen discharge at a high temperature.

(d) *Carbonization Variables*.—Under (d) the varia-

³Bull. 1, U. S. Bureau of Mines, "The Volatile Matter of Coal," 1910.

⁴Journal Chem. Soc. (London), 97, 1917. "The Volatile Constituents of Coal (1910)."

tions which occur in the first part of the carbonization bear a direct relation to the speed with which that part of the process is carried out. It is true that a higher or lower temperature will influence the rapidity with which decomposition takes place, but this is by no means the only factor. For example, with the same crucible and the same temperature, a higher volatile discharge will be recorded if the mass of coal is spread with a concave surface so that more of the coal is brought into contact with the metal. Or to reverse the conditions, a small 10-gram crucible will have less superficial contact with the metal than a 30-gram crucible. If in each case the coal is allowed to assume its natural shape with level surface, the larger crucible will discharge the larger amount of volatile matter. Again, the same 10-gram crucible will yield more volatile if the coal is spread around the sides, giving it a concave surface, and increasing the area exposed to the crucible. These four sets of conditions are illustrated in the following table:

It seems evident from the above data that the

conditions where in porcelain can be substituted for platinum.

Other influences, such as the presence or absence of free moisture, especially in lignites, the use of a muffle instead of a flame, etc., have been partially tested but not sufficiently to be reported upon at this time, further than to say that the Méker burner promises to afford a much more even temperature than the ordinary Bunsen burner; or rather, it delivers a large amount of heat instead of a small localized zone at the tip of a small flame. There is a decided advantage also in the larger volume of flame which more completely envelops the crucible and furnishes at the same time an atmosphere with but little oxidizing property.

It is not the purpose of this paper to make recommendations as to the best procedure since the whole matter is under consideration by the committee on revision of methods for coal analysis. It may be said, however, that the experiments indicate certain essentials, outlined as follows:

1. Definiteness of temperature.

TABLE IV.—SHOWING VARIATIONS DUE TO SPEED OF VOLATILIZATION.

Lab. No.	Kind of coal.	A. 30-g. plat. cruc. coal with flat surface. Per cent.	B. 30-g. plat. cruc. coal with con- cave surface. Per cent.	C. Compare B with A. Per cent.	D. 10-g. plat. cruc. coal with flat surface. Per cent.	E. 10-g. plat. cruc. coal with con- cave surface. Per cent.	F. Compare E with D. Per cent.
4389	Bureau County, Illinois.....	47.03	47.95	+0.92	45.82	46.48	+0.66
1889	Logan County, Illinois.....	42.94	44.65	+1.71	42.29	43.21	+0.92
213	Lignite, North Dakota.....	56.93	57.18	+0.25	55.61	55.44	-0.17
2775	Rock Island County, Illinois.....	46.02	47.44	+1.42	45.02	45.56	+0.54
1810	Franklin County, Illinois.....	38.39	38.72	+0.33	37.76	38.31	+0.55
2773	Anthracite	9.23	9.01	-0.18	8.58	8.67	+0.09
	Average			+0.78			+0.43

greatest source of variation resides in that part of the process which involves the distillation of the fat or heavy volatile portion of the coal. These variations also are due to seemingly small influences, as high as 1.7 per cent in one instance, in sample No. 1889, Table IV, being due to the disposition of the charge against the sides of the crucible. If comparison were made as between the large and the small crucible as in columns A and D, a variation of 1.21 per cent is shown in sample 4389, due to this cause alone. It is evident, therefore, that in standardizing this part of the procedure, more than the simple matter of temperature must be taken into account.

Other evidence, all in the same direction, has been obtained wherein a weighed amount of clean, ignited sea-sand was mixed with the coal. This procedure gives a coke of uniform texture and obviates any tendency on the part of the coke to swell. But the yield of volatile matter is consistently lower, owing to the small retardation of the decomposition processes. Another bit of evidence in the same direction is the use of a porcelain crucible which again retards the process and gives lower results by from one to two per cent. This reduction in yield with a porcelain crucible can be very largely counteracted by using a correspondingly higher temperature, but more data is necessary before a conclusion can be drawn as to the

2. The employment of a temperature not below 900° or 950°.

3. Use of a crucible of given size and shape.

4. A capsule cover fitting inside of the crucible and not on top.

5. The use of kerosene to moisten the charge.

6. If a burner is to be used, the Méker type has a great advantage in furnishing a larger volume of heat less localized than that of the ordinary Bunsen type.

7. A small crucible is preferable to a large one, as it is more readily enveloped completely by the flame of the burner and the coal mass is less subject to variations in form. This is very important in view of the large variables that may enter into the early stages of decomposition.

The American Minister Larz Anderson at Brussels has informed the Bureau of Manufacturers on the removal of the discrimination which has existed against American lubricating oils in connection with public tenders for supplies for the Belgian State railways. The specifications for supplies have in the past called for Russian oils, thus preventing American oils from competing. The action of the Belgian Government follows representations on the subject of American lubricating oils made by the United States Government.

THE VOLATILITY OF ZINC OXIDE.*

By O. L. KOWALKE.

Several years ago, in connection with some experiments on the electric smelting of zinc ores, the question arose whether zinc oxide was volatile or not. In the literature there seemed to be only general statements as to the temperatures at which zinc oxide was volatile, but no record of definite tests was found. Stahlschmidt¹ says: "Zinc oxide is infusible and is notably volatile at 970° C., and about 15 per cent more at 1054° C., and is rapidly volatile at a high heat."

After the present investigation had been completed, it was found that this question had been studied by Messrs. Doeltz and Grauman.² Their methods are about the same as in this work, but the results are somewhat different, as will be explained later.

APPARATUS.

Pyrometer: A carefully standardized and properly protected thermocouple of platinum and platinum-10-per-cent-rhodium and a galvanometer of Keiser & Schmidt served as the means of determining the temperatures attained.

Zinc Oxide: The zinc oxide employed was "Zinc Oxide, C. P.," obtained from E. H. Sargent & Co., and was not tested for its purity.

Furnaces: The first furnace used was of the granular carbon resistor type. The treating chamber was a magnesia crucible 4¾ in. (12 cm.) long, 1¾ in. (4.3 cm.) in diameter, walls ¼ in. (0.6 cm.) thick, closed at one end, and surrounded by a shell of Acheson graphite. All of it was imbedded in the resistor in a horizontal position, with the opening of the crucible through the wall of the furnace. This arrangement allowed the introduction and removal of the zinc oxide from the furnace in a convenient manner. The mouth of the crucible was closed with a magnesia disk through which the pyrometer and sight tube were inserted, and the whole was cemented up with asbestos fibre.

This type of furnace was very convenient, but trouble lay in the fact that there was danger of reducing gases coming through the wall of the magnesia crucible. This did happen, and the results were of no value.

The only type of furnace that did not introduce any reducing material was a tube furnace of the Heraeus form, wound with some high melting-point metal, such as "nichrome" or platinum. Such a furnace consisted of a tube of porcelain or "Marquardsche Masse," about 1 in. (2.5 cm.) in diameter and 10 ins. (25 cm.) long. A spiral of resistance wire was on the tube and connected to the terminals at the ends of the furnace. The annular space of about 3 ins. (7.5 cm.) between the tube and the casing of the furnace was filled with fossil flour to serve as heat insulator.

The electric current from a 110-volt circuit used for

heating the spiral of resistance wire was regulated by means of a bank of incandescent lamps, which proved to be a convenient method for control of the current and hence of the temperature.

The "nichrome" ribbon does very well for temperatures below 1100° C., but temperatures above this can not be maintained very long, as the metal oxidizes rather rapidly. The platinum foil can, of course, be heated to a higher temperature, but in this case the foil was so thin that it was not safe to go above 1400° C. In this connection it might be of interest to state that a thin platinum foil does not work well with alternating current, as the vibrations resulting from this power break the foil. Direct current is entirely satisfactory.

PROCEDURE.

The zinc oxide was placed in a boat about ¾ in. (0.9 cm.) wide, ¾ in. (0.9 cm.) deep and 3½ ins. (9 cm.) long. Before using a new boat or fresh zinc oxide for any test they were both first ignited in a Bunsen flame to a constant weight.

The boat with the weighed amount of zinc oxide was then put in the furnace, and the pyrometer so placed that the junction of the couple was at the middle of the boat. The end through which the pyrometer was inserted was cemented up with loose asbestos, and the other end was provided with a tube about ¾ in. (0.9 cm.) diameter, open at both ends, which served as a sight tube.

The furnace with its contents was now slowly heated to the temperature desired, kept there, and then finally allowed to cool slowly to the original temperature. The period of cooling was usually over night, after which the boat with its charge of zinc oxide was removed and weighed. The loss of weight was considered due to the volatilization of the zinc oxide. The weight of the porcelain boat was very constant, and any variations in its weight were applied to the apparent loss of zinc oxide.

RECORD OF TESTS.

With Resistor Furnace: Several runs were made with this furnace, but in all of them the zinc oxide apparently volatilized at temperatures below 1300° C. White fumes of zinc oxide were observed at the exit at temperatures varying from 1150° C. to 1240° C. in the several runs, and it will be noted that these are about the temperatures at which zinc oxide is reduced. There seemed to be no question that the carbon monoxide from the furnace came through the walls of the magnesia crucible and reduced the zinc oxide. These tests are thus of no value so far as this problem is concerned.

With Tube Furnace Heated by Metallic Ribbon: It was clear from the above tests that even a small amount of reducing agent must be kept out of the furnace. The tube furnace satisfies these conditions, and the results obtained are much more satisfactory. The results of the successful tests are given in tabulated form in Table I.

*Paper presented at the 21st General Meeting of the American Electrochemical Society, in Boston, Mass., April 18-20, 1912.

¹Ingall's "Metallurgy of Zinc and Calcium," p. 5.

²"Metallurgy," 1906, 212, 233.

TABLE I.

No. 1.			No. 2.			No. 3.		
Temperature, Degrees			Temperature, Degrees			Temperature, Degrees		
Time.	Centigrade.	Time.	Centigrade.	Time.	Centigrade.	Time.	Centigrade.	Time.
9.00	635	3.30	910	11.00	1,075			
10.00	1,165	3.44	1,190	12.00	1,260			
11.30	1,210	3.48	1,260	2.00	1,325			
12.00	1,240	3.50	1,290	2.30	1,360			
				3.30	1,370			
			No. 1.	No. 2.	No. 3.			
			Grams.	Grams.	Grams.			
Weight ZnO taken.....			1.0030	0.7560	0.9042			
Loss of ZnO.....			0.0102	0.0305	0.9040			
Per cent loss.....			1.01	4.3	100.0			

DISCUSSION OF RESULTS.

It appears from these tests that zinc oxide can be completely volatilized at temperatures from 1370° C. to 1400° C. In all of these tests the zinc oxide was exposed to the high temperatures for a considerable period of time, a condition not exactly comparable to smelting conditions.

The loss of zinc oxide increases rapidly with temperature rising above 1300° C., as shown in these tests. The loss seems, however, to be of a nature similar to the slow evaporation of water below the boiling point, but at temperatures above 1400° C. it appears reasonable to say that the volatilization proceeds rapidly.

This view is supported by the work of Doeltz and Grauman, who find that at 1400° C. a series of nine treatments, for periods of 10 minutes each, produced a loss of 13 per cent of zinc oxide. However, when zinc oxide was dropped on a platinum wire heated by a current of electricity to a bright red heat, the zinc oxide adhered tenaciously, and upon heating the wire to a white heat, above 1400° C., and near its melting point, a rapid volatilization of zinc oxide took place.

The painstaking assistance of Mr. Albert R. White in obtaining these data is hereby acknowledged.

The statistics of coal production in Maryland, which have been collected by Edward W. Parker, of the United States Geological Survey, in co-operation with the Maryland Geological Survey, show that the total production in 1911 amounted to 4,685,795 short tons, valued at \$5,197,066. Compared with the production in 1910, the output in 1911 showed a decrease of 531,330 short tons, or 10.2 per cent, in quantity, and of \$637,992, or 10.9 per cent, in value. Stimulated, as had been the other Appalachian states in 1910, by the strike of miners in the middle west, Maryland in 1910 increased her production nearly 1,200,000 tons over 1909, and a part of the markets secured at that time were held in 1911, but not sufficiently to maintain the tonnage of the preceding year. The coal fields of Maryland are not of wide extent and the production during the 90 years of their exploitation has been derived chiefly from the "Maryland Big Vein," an outlier of the famous Pittsburgh bed of Pennsylvania. This vein had a thickness of 10 to 13 ft. in the western part of Allegany County, Maryland, extending southward into Mineral County, West Virginia. Mining operations covering nearly a century have exhausted a large part of this great coal bed in Maryland, and during the three or four years preceding 1910 the produc-

tion of the state had shown a declining tendency, as some of the mines were being worked out.

The United Kingdom imports about 65,000 tons of rock asphalt annually. In 1910 the quantities bought from various countries, with their values per long ton, were as follows: From Germany 24,960 tons (\$11.33), France 11,985 tons (\$10.27), Italy 10,308 tons (\$9), British West Africa 15,421 tons (\$14), United States, 3,697 tons (\$20).

Through the merger of four of the largest concerns operating kaolin mines and refineries in the Zettlitz (Carlsbad) district the entire deposit is now controlled by two firms. The Zettlitzer Kaolinwerke A. G. has increased its capital from 1,000,000 to 7,500,000 crowns (\$203,000 to \$1,522,500) in order to absorb three independent firms, and is in a position to control the market. Kaolin from the Bohemian deposits has been sold for some years under a trust agreement and the present price is 64 crows (\$13) a ton in 1-ton lots. The property owned by the Zettlitzer Kaolinwerke includes the refinery at Sodan, the largest on the Continent. In connection with the independent firm it has secured deposits at Spittengrun, near Carlsbad, which will be available for the next 50 years at the present rate of output.

A demonstration, held at Plymouth, of a new method of defrosting meat is described in a report from the New South Wales Agent General in London. By this process frozen meat is thawed in a chamber so constructed that the atmospheric pressure can be regulated and excess moisture extracted without bursting the tissues of the meat. It is claimed that frozen beef and mutton can then be placed on the market in such a condition as to compare favorably in appearance with prime English meat. This demonstration was attended by representatives of the meat trade of Australia, Great Britain, the United States, and South America. The beef and mutton had been held in a temperature of about 18° for about three weeks after removal from the ship. It was then placed in the patent chambers (beef for 48 hours and mutton for 24 hours), in a temperature of 62°. Upon removal from the chambers the beef was compared with prime English beef and with a frozen quarter from Queensland treated under the old system. It compared favorably with the English meat and was far superior to the Queensland. It had a fine bloom, was free from mold, and there was an entire absence of "leakage." The kidneys and suet fat remained in the treated quarters and when cut were free from bone taint or bone odor. Quarters of treated beef and carcasses of mutton were cut up in the presence of the visitors with satisfactory results, defrosting having been thoroughly carried out. On the following morning the treated meat, cut and uncut, was inspected at the Smithfield Market and found to be still satisfactory and free from the drawbacks of frozen meat marketed in the usual way.

The CHEMICAL ENGINEER

HARRY McCORMACK, Editor.

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METHODS OF ANALYSIS.

There was published in the April number of this Journal the first of a series of articles on the laboratory of the Armour Institute of Technology methods of analysis. No originality is claimed for these methods. They represent the methods found most suitable for the students taking the course in Chemical Engineering, and they are also the methods employed in the Commercial Test Department of this institution.

Many chemists are troubled with the multiplicity of methods as found in the literature for the analysis of almost any material. It will take a man with considerable knowledge to select a method which gives accurate results and which will not consume abnormal length of time. The methods published are as employed by the editor, who has had some twenty years' experience in applying such methods to the analysis of various substances. The methods are given in the order in which they are presented to the students, beginning with the simpler analyses and extending to more complex substances later.

These methods are published with the hope that they will aid the practicing analyst in selecting a method where he is not perfectly familiar with the methods to be employed in examining the material submitted for his analysis and report.

RETIREMENT OF DR. WILEY FROM PUBLIC SERVICE.

There are few chemists in the country who have been brought more prominently before the public or who have done more to benefit the public than Dr. H. W. Wiley. It is believed that the only class of people who do not regret his retirement from public service are the manufacturers and venders of food products not complying in the strictest manner with the pure food law.

Dr. Wiley waged a long campaign to secure the adoption of our present pure food law and since the passage of this law he has been continuously on the alert to protect the interests of the consumer. He has always stood out against the use of all materials which might be termed "just as good as." He insisted that labels on food products should tell just what they were. In many instances this worked financial injury to those attempting to foist spurious articles on the public; this undoubtedly explains the hostility to him in some quarters.

There is no question that the retirement of Dr. Wiley will make it easier for such manufacturers. His successor, with the best intentions in the world, will be unable to successfully combat such practices as he will lack the intimate knowledge of such conditions as gained by Dr. Wiley in his long service as head of the Bureau of Chemistry.

REPORT OF COMMITTEE ON PROFESSIONAL CODE OF ETHICS.

The Journal of Industrial and Engineering Chemistry recently published a report submitted by the committee on professional code of ethics and presented at the Washington Meeting of the American Chemical Society.

The report follows:

Your committee beg to report that after a careful consideration of the subjects, it is their belief that a code of ethics should be formulated and adopted by the American Chemical Society.

There are many instances which can be cited of unethical practices among chemists, such as: misleading advertisements and interviews in papers and magazines; the lending of certificates for advertising uses; the misuse of our science for the purpose of perpetrating frauds on the public, such as the evasion of a standard of purity or the sophistication of a product; slovenly and unreliable work sometimes revealed by impossibly low prices for analytical tests; expert testimony of a character discreditable to the witness and to our profession; a lack of courtesy towards our fellow chemists; and in this respect we stand far below the medical profession.

The present committee of three should be retired, and a larger committee, of perhaps seven members, be appointed, representing the various branches of our

profession, and with power to draw up and recommend a code of ethics.

Such work should be done deliberately and with the greatest possible discussion, which can not fail to have a beneficial effect, in pointing out evil practices and elevating our standards of behavior.

This subject has already been discussed at Indianapolis, Louisville and New York, and we believe that each of the several sections would do well to devote one night to the discussion of this problem.

We do not think that for the present, at least, it will be possible or desirable for the American Chemical Society to attempt the enforcement of a code of ethics, still less to examine members with a view to certifying their competency as is done by the Institute of Chemistry of Great Britain; but we do feel that the adoption of a carefully worked out code of ethics, prominently displayed in our publication, would set before us the standard of professional conduct, which, as members of the American Chemical Society, we would be expected to follow, and which would greatly tend to emphasize our brotherly relations to fellow chemists and elevate the ideals of our profession.

(Signed) A. C. LANGMUIR,
C. F. McKENNA,
L. F. BROWN.

This report is about as noncommittal in the way of recommending something to be done as a committee report could well be. Nearly every chemist is familiar with the unethical practices all too common in the profession. It is not a question as to fact, but a question of what can be done to decrease such practice or if possible to prevent it.

The recommendation of this committee that a code of ethics be formulated and prominently displayed in our publication might accomplish something. Every chemist or chemical engineer knows, however, whether his professional conduct is as it should be or not. To some extent it may be a question of education and, insofar as this is the case, a publication of a recognized code of ethics would be beneficial.

The greater part of the unprofessional practices come, however, from men not lacking in knowledge of proper conduct, but lacking in integrity and at the same time familiar with the fact that they can proceed as they do without receiving the censure of the other members of their profession. It is usually true that such men are not at all prominent nor closely affiliated with the activities of the American Chemical Society. It is a regretted fact, however, that some of them are members of this society.

It should be possible to find some method of procedure by which the practice of such men can be brought to the attention of their colleagues in such a way as to discourage their unethical practices, and it is to be hoped that in time the society will appoint a committee to investigate these conditions and formulate some method of procedure by which this can be accomplished.

RECENT PATENTS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, 908 G Street, N. W., Washington, D. C.

- 1,019,102. Process of Manufacturing **Paraffin**. Julius Tanne, Rozniatow, Austria-Hungary, assignor of one-half to Gustave Oberlander, Berlin, Germany. Patented March 5, 1912.
- 1,019,230. Manufacture of **Formates**. Olivier Louis Andre Dubosc, Arman Die Luttringer, and Hector Dennis, Paris, France, assignors to Societe Le Camphre, Paris, France. Patented March 5, 1912.
- 1,019,377. **Heat-Producing Compound**. Clarence G. Smith, Cleveland, Ohio, assignor to Henry J. Haber, Pittsburgh, Pa. Patented March 5, 1912.
- 1,019,393. **Boron-Carbon Alloy**. Ezechiel Weintraub, Lynn, Mass., assignor to General Electric Company, a corporation of New York. Patented March 5, 1912.
- 1,019,415. **Paint Compound**. William N. Blakeman, Jr., New York, N. Y. Patented March 5, 1912.
- 1,019,431. **Decarburized Silicon** and Method for Making the Same. John T. H. Dempster, Schenectady, N. Y., assignor to General Electric Company, a corporation of New York. Patented March 5, 1912.
- 1,019,526. Compound or Alloy of **Titanium and Silicon**. Auguste J. Rossi, Niagara Falls, N. Y., assignor to The Titanium Alloy Manufacturing Company, New York, N. Y., a corporation of Maine. Patented March 5, 1912.
- 1,019,527. Process for Producing the Alloy of **Titanium** with Zinc. Auguste J. Rossi, Niagara Falls, N. Y., assignor to The Titanium Alloy Manufacturing Company, New York, N. Y., a corporation of Maine. Patented March 5, 1912.
- 1,019,528. Process for Producing Alloys of **Titanium** with Ferrometal. Auguste J. Rossi, Niagara Falls, N. Y., assignor to The Titanium Alloy Manufacturing Company, New York, N. Y., a corporation of Maine. Patented March 5, 1912.
- 1,019,529. Process for Producing the Alloy of **Titanium** with Lead. Auguste J. Rossi, Niagara Falls, N. Y., assignor to The Titanium Alloy Manufacturing Company, New York, N. Y., a corporation of Maine. Patented March 5, 1912.
- 1,019,530. Process for Producing the Alloy of **Titanium** with Tin. Auguste J. Rossi, Niagara Falls, N. Y., assignor to The Titanium Alloy Manufacturing Company, New York, N. Y., a corporation of Maine. Patented March 5, 1912.
- 1,019,531. Method of Treating **Aluminum**. Auguste J. Rossi, Niagara Falls, N. Y., assignor to The Titanium Alloy Manufacturing Company, New York, N. Y., a corporation of Maine. Patented March 5, 1912.
- 1,019,569. Method of Making **Boron** and Boron Alloys. Ezechiel Weintraub, Lynn, Mass., assignor to General Electric Company, a corporation of New York. Patented March 5, 1912.
- 1,019,666. **Paint and Varnish Base**. Rudolph Lender and Albert Koch, Neu-Babelsberg, Germany. Patented March 5, 1912.
- 1,019,705. Process of Manufacturing Carbureted **Hydrogen Gas**. William J. Watkins, Fort Worth, Texas, assignor to O. G. Hurdleston, Fort Worth, Texas. Patented March 5, 1912.
- 1,019,708. Process of Treating **Copper Ores** or Copper-Ore-Mill Tailings. John W. Bennie, Clifton, Arizona. Patented March 5, 1912.
- 1,019,746. **Fuel Composition**. Benjamin Appel and Samuel S. Goldman, St. Louis, Mo. Patented March 12, 1912.
- 1,019,829. **Paint and Varnish Remover**. James S. Patty, Chicago, Ill. Patented March 12, 1912.

- 1,019,854. Process of **Unhairing Hides** and Skins. Louis Stern, Newark, N. J. Patented March 12, 1912.
- 1,019,965. Treatment of **Metals**. William H. Kelly, Los Angeles, Calif. Patented March 12, 1912.
- 1,020,121. **Calcium Salt** of Acetyl Salicylic Acid and Process of Making Same. Rudolph Berendes, Elberfeld, Germany, assignor to Farbenfabriken vorm. Friedr. Bayer & Co., Elberfeld, Germany, a corporation of Germany. Patented March 12, 1912.
- 1,020,124. Hydraulic **Cement**. Frederick W. Brown, Florence, and George W. Bartholomew, Denver, Colorado. Patented March 5, 1912.
- 1,020,219. Process of Purifying Sugar. Juan Ost. Buenos Aires, Argentina. Patented March 12, 1912.
- 1,020,224. Process for Recovery of **Vanadium**. Byramji D. Saklatwalla, Bridgeville, Pa., assignor to The American Vanadium Co., Pittsburgh, Pa., a corporation of New Jersey. Patented March 12, 1912.

PROPOSALS FOR LABORATORY EQUIPMENTS AND SUPPLIES.

City of Fargo, N. Dak.

Sealed bids will be received at the office of the City Auditor of the City of Fargo, N. Dak., until the hour of 5 o'clock in the afternoon of the 3d day of June, 1912.

First—For furnishing equipment for filtration plant chemical laboratory and supplies therefor.

Second—For furnishing equipment and apparatus for the chemical and bacteriological laboratory in the Milk and Meat Inspector's office in said city.

Such proposals shall be carefully sealed and plainly marked "Proposals for Filtration Plant Laboratory" or "Proposals for Milk and Meat Inspector's Laboratory," as the case may be.

Each proposal shall be based upon and refer specifically to schedules which will be furnished upon application by Mr. F. L. Anders, City Engineer, Fargo, N. Dak., and by Dr. I. L. James, Meat and Milk Inspector, Fargo, N. Dak.

Each proposal shall be accompanied by a certified check in the sum of \$500 to insure execution of contract, if awarded.

The successful bidder will be required to enter into contract with the city for such equipment and furnish a bond in a sum equal to the amount of such contract, indemnifying the city against delay in delivery, or materials below grade.

The City Council reserves the right to reject any and all bids, or any part of a bid, and to accept any bid or part thereof.

Dated this 8th day of May, 1912.

E. R. ORCHARD,
City Auditor, Fargo, N. Dak.

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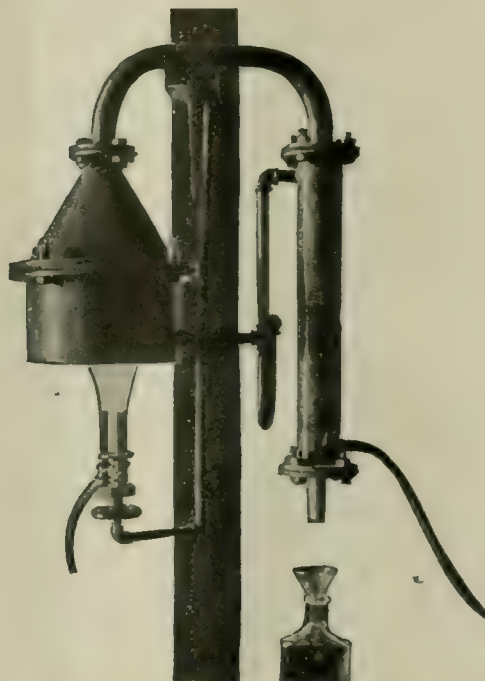
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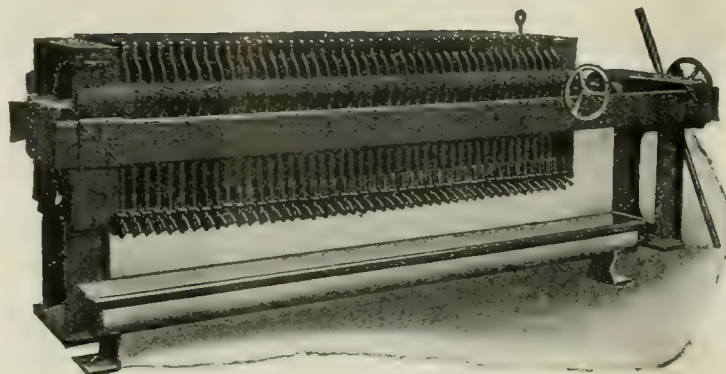
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Meade's "Design and Equipment of Small Chemical Laboratories" is a book which every assayer and mining company ought to get and read before ordering an assay and chemical outfit. There is more unnecessary "junk" accumulated and more essential things wanting as a result of ordering laboratory equipment than in almost any other department of the ordinary mine. This is because the man doing the buying, as a rule, does not know the difference between a pipette and a rubber cork. A little book like Richard K. Meade's will furnish the information both for ordering the equipment and designing the laboratory.—*MINING SCIENCE*, Sept. 17, 1908.

Meade's "Design and Equipment of Small Chemical Laboratories" is, from cover to cover, excellent in its advice and suggestion, being the product of a finished chemist who knows the needs of the shop and school. Many an assayer would do well to follow the hints given in this book on sampling and preparation of samples.—*MINING AND SCIENTIFIC PRESS*, Sept. 19, 1908.

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FREE LIME IN PORTLAND CEMENT.*

By H. E. KIEFER.

It is to be regretted that the majority of chemists engaged in the manufacture of Portland cement have very little time for research work. Some of us have considerable time for experimental work, but the time and money spent are expected to produce commercial results rather than contribute to the stock of purely scientific knowledge. The latter we are compelled to leave to the research chemist, and as he usually lacks a practical manufacturing experience we may be able to supply a few facts and suggestions.

One of the most troublesome arguments which the cement chemist has to meet is on the subject of *Free Lime*. We hear it discussed by chemists and engineers and attribute all kinds of defects in the cement to it, yet it is very questionable whether any of us have a well grounded theory for the position we assume. We manufacture a product to meet certain specifications and when it fails in any of these we look for the cause and a remedy from a practical rather than a theoretical point of view, using theory only to facilitate results. A few things we know and many more we believe, hence we shall state first the general knowledge and follow it up with the theory and then add a few observations which may furnish suggestions for research chemists.

Constancy of volume is one of the requirements of practically all specifications. The test is made by subjecting a hardened pat to five hours' boiling in water in a loosely covered vessel or to the steam above the water in such a vessel. If the pat comes out sound and hard, with no signs of warping, checking or disintegration, the cement is considered sound. On the other hand, if it becomes soft, or warps or cracks on the edges, it is considered unsound. From this point the theory begins. The explanation is that a failure to pass the test is due to free lime. Various quantitative methods have been suggested with a view of determining it, but so far as the writer knows none has ever given satisfaction. Microscopic tests have been suggested, but these likewise fail to be of any practical value. Some observations made in our laboratory lead to the belief that if free lime is a real cause it is not

the only one, as there is a physical side which must be taken into consideration.

Le Chatelier says that if 1 per cent of freshly calcined lime be added to a sound cement it will render it unsound. With this as a starting point, five well known American brands of Portland cement, which passed the boiling tests as received, were taken and the above percentage of lime, freshly calcined over a blast lamp, immediately pulverized and added to the cement. None of them failed on the test. Larger quantities were then added, and with one brand 25 per cent of freshly calcined free lime was required before the cement failed on the boiling test. The authority mentioned fails to say how finely the lime should be ground before adding to the cement, but it was presumed it should be at least as fine as the cement, hence it was quickly put through a 100-mesh sieve. The lime was obtained from a pure limestone at the highest temperature of a blast lamp. It might have been better to have used calcined filtrate as a starting point, but while these results are interesting, later tests showing the amount of water absorbed in passing from an unsound to a sound state shed a different light on the subject. The results of the tests are given in tabulated form.

In Table I are also given the analyses and the fineness of the cements to which reference will be made later. In one column are the results with lime sieved through a 100-mesh sieve and the cement as received, and in another column the cement after passing through a 200- and lime through a 100-mesh. It is necessary to explain that where "Boiled O. K." is used, it means the cement passed the test satisfactorily. To show degrees of soundness we use "Boiled 95 per cent" to mean checked slightly; "Boiled 90 per cent" to mean checked and softened slightly; "Boiled 85 per cent" to mean softened considerably; and "Boiled 80 per cent" to mean disintegrated entirely. These are only relative terms but they serve to indicate different degrees of soundness.

It will be noted in every case that the fineness of the cement played an important part, as when the particles coarser than 200-mesh were removed, the cement stood larger additions of lime. The inference is that the fineness of the cement, the fineness of the lime and its degree of fusion play an important part. Unfortun-

*A paper presented at the 45th annual meeting of the American Chemical Society, Washington, D. C., December, 1911.

nately, brands B, C, D and E were all over one year old when tested, but it will be noted that brand A, one month old, 85½ per cent passing a 200-mesh sieve, permitted 10 per cent greater addition of freshly calcined lime than the same brand two months old, 82.4 per cent fine and 2½ per cent more than the same per cent fine four months old, and that four coarser cements over a year old permitted the addition of less lime than the finer cement at two and four months.

Following this line and believing that the fineness of cement plays another part, a sample of cement 80 per cent passing a 200-mesh sieve, which failed badly on the boiling test, was ground in a mortar to

in a small room where it was presumed the atmosphere was fairly dry, owing to the presence of a number of trays of cement and lime on which experiments were being made, gave similar results.

Table II gives the results of the average of five different samples of cement in each case, each treated in the following manner: grinding in a mortar, grinding in a tube mill and sieving. It will be noticed that the sample which was merely sieved to increase the fineness required a higher fineness as indicated by the 200-mesh sieve than the reground samples. This, of course, was to be expected:

TABLE I.

No.	Brand and age.	Fineness. Percentages.		Cement as received and CaO through 100-mesh percentages		Cement through 200 mesh and CaO through 100-mesh percentages.	
		100-mesh.	200-mesh.	(a) CaO.	(b) H ₂ O.	Boiled.	(a) CaO.
1	A 1 mo...	95.2	82.4	5.0	27.0	O.K.	12.0
				6.0	28.0	90	34
				10.0	30.0	O.K.	O.K.
1	2 mo...			12.5	33.0	95	15.0
				15.0	35.0	80	35
				12.5	33.0	O.K.	39
				15.0	35.0	95	80
1	4 mo...			17.5	36.0	90	20.0
				20.0	38.0	80	39
2	A 1 mo...	97.5	85.5	25.0	45.0	O.K.	90
				(c)			
3	B 1 yr...	96.0	79.0	5.0	27.0	O.K.	8.0
				6.0	27.5	95	30
				7.0	28.0	90	33
4	C 1 yr...	93.0	75.4	6.0	27.0	O.K.	8.0
				7.0	27.0	90	30
5	D 1 yr...	96.8	78.6	6.0	27.0	O.K.	8.0
				7.0	27.0	95	31
				12.0	29.0	O.K.	36
6	E 1 yr...			15.0	30.0	95	12.0
							29
							O.K.
							15.0
							31
							95
							17.5
							33
							80

(a) Per cent of lime added.

(b) H₂O refers to the water used in making the pats.

(c) Greater amounts of lime made the pats too soft to be boiled after 24 hours.

ANALYSIS OF CEMENTS.

No.	1.	2.	3.	4.	5.	6.
Loss on ignition ¹	3.08	2.80	4.60	5.19	3.20	6.27
SiO ₂	21.28	20.80	19.24	20.26	22.00	19.68
R ₂ O ₃	9.02	9.50	10.52	9.32	9.00	11.00
CaO	62.24	62.40	60.98	60.09	62.30	58.60
MgO	2.68	2.75	2.78	3.34	2.64	2.18
SO ₃	1.61	1.56	1.55	1.54	1.23	1.54

¹The high loss on ignition in several of these brands is due to the long seasoning in bags.

85 per cent fine and it showed improvement. In another portion ground 90 per cent fine, the improvement was more marked and in a portion ground 95 per cent fine the boiling test was perfect. We repeated this on various samples of cement with similar results. Thinking that possibly the free lime became hydrated from the moisture in the air while being ground, similar experiments were made by regrounding in a laboratory tube mill with a rubber gasket, so that the negligible amount of moisture in less than ½ cu. ft. of air would have a negligible effect on hydrating the free lime in 15 lbs. of cement used in the test. Results were similar. Sieving to various degrees of fineness

TABLE II.—EFFECT OF FINENESS ON THE BOILING TEST.

	By re-grinding in mortar. Boiling test.		By re-grinding in tube mill. Boiling test.	Fineness regulated by sieving. Boiling test.
	Per cent.	Per cent.		
81 per cent passing 200 mesh, as received	80	80	80	80
After bringing up to 85 per cent fine	85	85	85	80
After bringing up to 90 per cent fine	90	90	90	85
After bringing up to 95 per cent fine	O. K.	O. K.	O. K.	90
After bringing up to 100 per cent fine	O. K.	O. K.	O. K.	95

It might be argued that the free lime was largely in the particles removed by the sieve, but this is offset by the tube mill experiments which were of exactly the same cement except as to fineness, as nothing was added or removed, and if the failure when 80 per cent fine was due to free lime, the same free lime was present when it was 95 per cent fine, and if checking is due to free lime, this free lime in the 95 per cent fine was in a fine enough physical condition to become hydrated immediately on adding water when making the pat, or at least to become hydrated before the set had taken place. In the coarser samples it is possible that the free lime (if it is such) was present in the fused, glassy, coarser particles in such a way as to prevent its hydrating before the set had taken place, and the expansion took place on boiling the pat after it had hardened. The inference here is plainly that the degree of fineness is an important factor. The foregoing experiments apparently lead to the conclusion that a fair proportion of free lime is not injurious to a Portland cement if its physical condition is such as to permit it to be hydrated before the set has taken place. Hydrated lime is added to Portland cement with beneficial effect in some cases and it matters not if the hydrated lime is added afterwards or free lime is in the cement when used, provided it is in a condition to be readily hydrated, assuming that all other conditions of balancing the chemical composition and manufacturing details are properly regulated.

It is often noted that a sample of cement which fails to pass the test one day may pass it very satisfactorily several days later, and it has frequently been noted where the change from very poor to very good took

place in 24 hours. In some cases where the pats completely disintegrated on boiling, the cement became sound in three or four days, while with several brands samples have required thirty days or more to become thoroughly seasoned.

An effort was made to find what change took place in the ultimate chemical composition when a cement passed from an unsound condition to a sound one. If it is due to a hydration of the lime by atmospheric moisture, then the amount of moisture absorbed would be a gage to the amount of free lime which had been hydrated, assuming (without any sound theoretical reason) that all the moisture taken up would go to hydrating lime and none of it enter into the complex reactions which take place when larger amounts of water are used. A number of experiments were made by determining the loss on ignition on unsound cements and making the same test after the cement became sound. A more correct method would have been to absorb the water given off on ignition, as it is well known that cement absorbs carbon dioxide on seasoning and this also is given off on ignition, but a glance at the results will show the relatively small total difference that even if we assume it all to be water used in hydrating lime the amount of lime hydrated is comparatively small:

6 tests showed a difference of 0.45 per cent in loss on ignition between the unsound and sound condition of the cement.

6 tests showed a difference of 0.75 per cent.

6 tests showed a difference of 0.90 per cent.

Realizing the inaccuracy of the method, another set of experiments was conducted as follows: The unsound cement was placed on cover glasses and carefully weighed. This was placed on a rack under a bell-jar. A tray of water was placed below it and the whole set on an iron plate over a Bunsen burner. The bottom was sealed by piling finely pulverized flint (100-mesh and finer) around the lip of the jar so that the air could not be renewed during the test. The temperature was raised to 150° F. and kept there from periods ranging from one to twenty-six hours. A very great number of these tests were made and it was found that at 26 hours' heating, three samples of different cements absorbed 1.27 per cent, 1.84 per cent and 2.02 per cent moisture. All of these, as expected, passed the boiling test perfectly.

Repeated trials were made to determine the minimum amount of absorption necessary to pass from an 85 per cent failing cement to a perfect test:

3 tests showed 0.10 per cent was sufficient.

5 tests showed 0.19 per cent was sufficient.

3 tests showed 0.24 per cent was sufficient.

3 tests showed 0.27 per cent was sufficient.

Whether these are the minimum amounts is open to question, as a number of tests showed practically no absorption, yet it is apparent that moisture is essential to seasoning. Unsound samples kept in sealed jars a year still remained unsound, and samples heated

to 150° F. in dry air remained unsound, yet the above shows that a trifling amount of moisture produced the desired result. Moisture is essential and heat accelerates the action, as to be expected. At lower temperatures it is necessary to absorb considerably more water to get results than at 150° F. Coarse cements required more water and the problem becomes more complicated where the degree of burning of the clinker, the fineness of the raw material, and other manufacturing factors are taken into account.

Referring to the above tests where the minimum water was absorbed, it becomes apparent that in those cases, assuming all the moisture absorbed went to hydrating free lime, the maximum amount of free lime exerting the injurious influence could not have been over 0.31 per cent. Compare this with various amounts of free lime added, shown in Table I. It may be possible that the destructive expansion in the case of three cements requiring only 0.1 per cent water in seasoning was caused by the hydration of its equivalent of 0.31 per cent CaO, but it seems more probable that a physical explanation must also be considered in connection with it, for reasons briefly stated as follows:

Lime calcined at highest heat of a blast lamp is not injurious to soundness when added in reasonable amounts to Portland cements. Lime calcined at the temperature attained in a rotary kiln does not become fused, hence when pulverized with the clinker should hydrate readily on the addition of water.

In burning of Portland cement clinker, small particles of free lime may be encased in the fused mass of silicates, aluminates, etc. If subsequent grinding reduces this glass to a finely enough divided state, this lime will hydrate on addition of water and have no injurious effects. If free lime is the cause of disintegration, it seems that the state of fusion of the surrounding glassy clinker is directly responsible for it.

It is claimed that over-limed cements are most apt to fail on this test. It may be possible that owing to their being more difficultly fusible and requiring a higher temperature in the kiln, that a more glassy mixture envelops the free lime. This furnishes room for microscopic study.

Under-burned cements may fail on this test. Free lime is given as the explanation of this.

If free limes is the real cause, then the fact that as little as 1/10 of one per cent of moisture will rectify many bad cases, leads to the belief that the phenomenon of seasoning is not so much one of hydrating free lime as it is a decrepitation process in which heat and moisture break up glassy particles, putting the lime in a physical condition to be hydrated, but not necessarily hydrating it. Acting on this idea, it was believed that cements become finer with age. A number of tests seemed to confirm this, but the breaking of the small per cent of coarser particles into finer ones takes place so slowly that differences of only one and two per cent were obtained in sieving, which may not be suf-

ficient to offset the possible personal error in the sieving process. To get at the hydrating or decrepitation results, whichever it may be, only the residues left on a 200-mesh sieve were taken and sieved until no more would pass. These were exposed to air and moisture and again sieved each week. The following table shows the fineness of a sample of cement, part of which was exposed to air and part kept in a sealed jar for varying periods. Residues from the same cement were placed in an open-jar and starting with nothing that passed a 200-mesh sieve, samples were sieved at various times, showing the per cent passing the 200-mesh after decrepitation had taken place.

TABLE III.—SHOWING FINENESS ON A 200-MESH SIEVE.

	Sample exposed to the air.	Sample kept in a sealed jar.	Sample of residues kept in an open jar.
	Per cent.	Per cent.	Per cent.
Starting point	84.6	84.6	0.0
After 14 days.....	85.0	85.0	5.0
After 33 days.....	85.8	85.0	5.6
After 49 days.....	86.0	85.4	6.0
After 91 days.....	86.0	85.4	7.6
After 107 days....	86.2	85.6	7.6

As was to be expected, the sample kept in air increased in fineness more rapidly than the one in the sealed jar, and while sieving tests are subject to some variation and inaccuracies, these samples were tested on the same sieve by the same man and by the same method, hence the personal error is probably about the same in each case. The results of the samples exposed to air might be explained by the theory of hydration of free lime, but those on sample kept in a sealed jar must be explained by a physical theory of disintegration.

SUMMARY.

While the work on this subject is by no means complete, it represents the results of some hundreds of tests and at the present time points to the following as worthy of consideration:

1. Only a thin film on the coarser particle of cement enters into the reactions on the setting of the same.
2. These coarser particles become finer with age.
3. The disintegration of these particles improves the soundness.
4. That if free lime is the cause of destructive expansion, three-tenths of one per cent or less is sufficient to manifest itself.
5. That cases were noted where practically no absorption of water took place, hence cannot be explained by the hydration of free lime.
6. Cement kept in a sealed jar becomes finer with age, thereby indicating a mechanical decrepitation, which, as tests show, becomes more pronounced in the presence of moisture.
7. Carbon dioxide from the air, while it may aid in seasoning, is not essential, as shown by several series of tests.
8. That increasing the fineness of any particular sample of unsound cement improves its quality in this respect.

9. With the foregoing data, it appears that the theory of free lime as the sole cause of unsoundness is not well founded.

10. Expansion may be due principally to physical strains in the coarser particles.

11. Any theory of expansion on a purely physical basis seems inadequate, inasmuch as pats may frequently remain in boiling water several hours or more before destructive expansion becomes manifest. If it were merely the different rates of expansion, one would expect the rupture to take place shortly after the boiling begins.

12. With the data in hand at present, a possible theory presents itself as follows: Seasoning of an unsound cement consists of decrepitation of the coarser particles, caused by or accelerated by heat and moisture, and that the moisture need not be in sufficient quantities to hydrate the free lime, but merely to render the coarser particles sufficiently fine to permit hydration before the set has taken place.

13. Le Chatelier claimed tri-calcium silicate to be the essential constituents of Portland cement and free lime as the agent destructive to soundness. Unger obtained *vitrified* tri-calcium silicate which disintegrated (seasoned), yet hardened well, while a *fused* tri-calcium silicate was unsound. This would indicate that if free lime is present in Portland cement, it is in the glassy unground particles.

14. O. Schott denied the existence of tri-calcium silicates, tri-calcium aluminates, and tri-calcium ferrites in Portland cement, yet fused mixtures of these compositions showed the characteristic destructive phenomena found in unsound cements and which he attributed to free lime.

15. Michaelis claimed burning at too high temperatures produced unsound cements. Microscopic examinations of clinkers show a different physical structure of that from a rotary kiln and that burned at lower temperatures. The contradictory results obtained by investigators, both of synthetical mixtures and actual clinker, seem to be due to different degrees of fusion.

16. Shepherd and Rankin have demonstrated the existence of calcium tri-silicate, but the real cause of expansion is yet not conclusively proven.

17. What is needed now, in addition to the excellent work of the authorities herein mentioned and others unmentioned, is an investigation which will link together our knowledge on purely theoretical constitution of Portland cement clinker and the chemical and physical constitution of a commercial Portland cement, and further show what changes take place in passing from an unsound to a sound state.

The mine production of gold in Alabama in 1911 was 915.06 fine ounces, valued at \$18,916, and that of silver 171 fine ounces, valued at \$91, according to H. D. McCaskey, of the U. S. Geological Survey. These figures show a decrease of \$14,617 in the gold output and of \$54 in the value of the silver.

SOME RECENT DEVELOPMENTS IN WOOD DISTILLATION.*

By THOS. W. PRITCHARD.

In taking up the subject of wood distillation, I wish to say in the beginning that, like every one else, I am subject to correction and am anxious to profit by the experience of others. It is only by so doing that we accomplish anything. There have been many improvements in the art of wood distillation since I first began the work, and I know of no industry which, in so short a time, has made such marked strides and which merits so much investigation and criticism.

In 1904 I prepared a paper for the *Scientific American Supplement*, in which I gave credit for the first commercial work in the distillation of pine wood to James Stanley, who built a small commercial plant in Wilmington, N. C., in 1872. This plant was not a success in the hands of Stanley, and was shortly after taken over by two gentlemen of Danish birth, who were somewhat familiar with similar work which was being carried on in their Motherland. One of these men is still living and is actively engaged in the work today. I speak of Mr. L. Hanson, who is president of the Spirittine Chemical Co., of Wilmington, N. C.

It is rather a striking coincidence that the first, and I may say the last plant, has been built in Wilmington, and the last one within a few feet of the former location of James Stanley's plant. This last plant, which is by my process, I shall describe later.

The process, as started by Stanley and carried out by Mr. Hanson, was the old crude method of destructive distillation, which consisted of a series of retorts with condensers attached, set up in brick work with furnaces beneath. The wood was placed in the retorts and the doors closed, fires started in the furnaces and kept up until distillation ceased; the retorts were then allowed to cool and the charge was withdrawn. No attempt was made to control the temperature during distillation and it was not until years later that the possibilities of varying products, depending on the temperatures, were thought of. By this old method, many different degrees of heat existed in the retort at the same time, and it was a noticeable fact that the top of the retort was many degrees hotter than the bottom or sides; the loss of heat was very great as it was necessary to heat up the brickwork before distillation started. There was no attempt at first to refine or separate these products; they were pumped into storage tanks and used for the preservation of timber, a creosoting plant having been built nearby, and the creosoting of timber was a part of the company's business.

I do not believe that any one, at this time, even thought of the possibilities of there being turpentine in the products of distillation. I can well recall the time when such a theory would have been hooted at.

I believe that we can safely give credit to the steam process people for the possibilities of the turpentine extraction from fat pine wood. I do not remember its production prior to their activities, and certainly not of good quality and in commercial quantities. This steam process with its variation held out many possibilities to us all at first, but I regret to say that, from my own observation, it has not proved commercially successful, save in a few cases.

Within the last few years still another process has been evolved, which, while not new, still, as applied to the extraction of the products from pine wood, was novel. I refer to the solvent process, for which great things are claimed.

By this process the wood to be treated is first shredded, or hogged, as it is called, and then subjected to the solvent action of naphtha or some other volatile solvent. The solvent combines with the resinous extracts and the resultant liquid is then drawn off and subjected to a fractional distillation. The solvent is recovered and the products are then refined. The solvent process is claimed by many to be the most profitable, and I know that large sums are being spent for the erection of plants using this process. I have always held, however, that there is but one method for the utilization of wood waste in the form of fat light wood; and that is to completely utilize the raw material. In no other industry would we find such a condition as exists where the steam process and the solvent process are in operation.

The taking of a raw material and the extraction of but a proportionately small part of its valuable contents and then throwing the remainder away, is a poor proposition, no matter how you look at it. I believe that every man who has ever turned his attention to this art, has realized from the beginning that the one great essential to be sought was temperature control during all times of the distillation. Many methods have been tried to solve this question, and I feel reasonably sure that it has at last been successfully worked out.

I refer now to the plant I have just completed for the National Wood Distilling Co., of which I am an officer. In describing this plant and the method used, I ask that I be allowed to indicate the weak points in the other processes, as each of these was of assistance to me in developing the new and successful process we have.

Let us take up the old destructive process and see how it bears a rigid analysis: First, for its good points (and I wish to say here that nearly every plant that has been a financial success has been of this type), the destructive process does utilize the raw material and it does produce far greater yields than any other process, the average production from a cord of good wood by the old destructive process being approximately 20 gals. of turpentine, 10 gals. of light oil and 70 gals. of heavy oil, with a residue of 25 bushels of charcoal to the cord. I do not include either alcohol or acetic acid,

*Paper read before the New York Section of the Society of Chemical Industry, March 22, 1912, and reprinted in the *Journal of Industrial and Engineering Chemistry*.

as their value is slight and varied, and I may say that very few plants distilling resinous woods have found it of advantage to utilize these products.

The first cost of this style of plant is not great in comparison with others, and the expense and difficulty of hogging wood is not a factor.

The weak points in this process are, however, serious defects: First, the lack of temperature control in the retort results in the formation of all sorts of compounds which distil with the turpentine and contaminate it; and this same lack of heat control results in a large percentage of the heavy products being burned in the retort. Any one who has ever operated a plant of this type will readily recall the deposit of carbonized matter which has to be cut out of the retort after a short usage. Secondly, the very high temperatures to which the average destructive plant is subject means a comparatively quick wear-out and very heavy upkeep, as well as an enormous waste of fuel. Third, the fire risk in this style of plant is very great, so high in fact, that no insurance company will accept a plant of this type as a risk.

In summing up the good and bad points we may say that the old style destructive process gives us good yields at comparatively low cost, but the products are of inferior quality, the cost of maintenance high and the fire risk great. In addition to this is the factor of time, as it takes very much longer to handle a quantity of wood by this process than by others.

In considering the steam process, we must give it credit for the quality of turpentine produced, and for the essential idea in wood distillation, the temperature control. We must, however, admit that a weak point in this process is the very small proportionate yield of products; secondly, that it does not utilize the raw material to the fullest extent, as a major part of the products of the wood are not extracted, thus necessitating the use of an enormous quantity of raw material to accomplish any great results.

There have been all sorts of claims as to the quantities produced by this process, but after very careful investigation, based on the report of men who are engaged in this line of work, I am forced to the conclusion that from 6 to 15 gals. of turpentine, and from 2 to 4 gals. of pine oil is the minimum and maximum yield for a cord of fat wood, the variations in quantity being due to the difference in quality and treatment.

The expense of production by the steam process is high; the waste of raw material is enormous and without reason. We may, therefore, grant to the steam process an excellent quality of products, with safety of operation so far as fire is concerned, and at the same time we must condemn it for the poor yields, cost of operation and waste of raw material.

Within the last few years still another process has been evolved. I refer to solvent process, for which great things are claimed. I am inclined to think from what I can learn that the solvent process possesses considerable advantages over the steam process in quantity

of production. I also believe that the quality of the turpentine is equally as good, and this process also produces a good yield of rosin. There is still, however, the objectionable feature of a very high fire risk, comparatively high cost of operation and failure to completely utilize the raw material.

The ideal process for the distillation of wood, we may then admit, must possess the following essential features: First, definite control of the temperature during the entire process of distillation; Second, a maximum yield of products; Third, products must be of good quality; Fourth, cost of operation must be comparatively low; and Fifth, the fire risk must be minimized as far as is possible.

I am going to try to describe a plant which we have recently built in Wilmington, N. C., within a few feet of the original plant of James Stanley.

When I first began work on wood distillation, I realized that temperature control was the one great issue. I tried experiment after experiment to achieve this, and at last discovered that by utilizing the old chemical process of the oil bath, I could get very definite temperature control at comparatively high temperatures. I had great difficulty for a long time in getting an oil which would stand repeated heating without cracking. I finally found, however, a very high fire-test petroleum cylinder stock, which could be heated to 600 or 700° F., without trouble, provided air was excluded. With this fact as a starter I developed our present process, which I will now try to describe.

I can best do this perhaps, by first describing a miniature plant complete, which I had built last year, and in which I ran continuously 96 charges. In the construction of this small plant, I used two pieces of pipe; the inner shell was 8 ins. in diameter by 24 ins. in length; the outer shell enclosed this, leaving an intermediary space of $\frac{1}{2}$ in. The ends of this space, of course, were tightly closed. From the inner shell an outlet pipe passed through the space and through the outer shell and connected with an ordinary worm, the condenser. Into the bottom of the outer shell at one end entered a $\frac{1}{2}$ -in. pipe, with the take-off at the bottom at the other end. Connected with this entrance pipe was a small gas hot-water heater, and from the bottom of this hot-water heater, a pipe led to a small rotary pump, and from the pump to a small steel storage tank. The outlet pipe from the bottom of the outer shell opposite end of the inlet pipe led directly to the top of this storage tank, which was enclosed. By means of the small rotary pump, the bath oil contained in the storage tank was forced through the gas hot-water heater, taking the place that would originally be occupied by the water in the same, and from there went into the intermediary space entering at the bottom, and was circulated around the inner retort, finding its outlet at the bottom of the outer shell farthest away from the inlet, from there passing back to the storage tank through the pump around the retort and so on, thus

keeping a continual circulation. Between the inlet pipe and outlet pipe I had a pipe of similar size connected with suitable valves so that the oil could be by-passed and the retort circulation completely cut off. I also had a reserve tank filled with cold oil, which allowed me to introduce cool oil into the circulation at any time. By means of increasing or decreasing the speed of the pump, opening or closing the valves used by passing or introducing cold oil into the circulation, I found it entirely practicable to control the temperature absolutely.

We used in this small retort 20 lbs. of wood at a charge, and estimating the weight of a cord of good rich wood at 4,000 lbs., we had no trouble in getting a pretty accurate approximate average of the production by this process. I must confess that the results of this experimental plant were far beyond our most sanguine expectations. We kept a record of every charge and our average for 50 charges was 36 and a fraction gallons of water white turpentine, 10 gals. of light oil, and 125 gals. of heavy oil.

I have with me one or two of these record sheets which I shall be glad to show. We found that we had no trouble whatsoever in getting complete and uniform carbonization, so complete, in fact, was the heat distribution by this method that a solid stick of timber 8 ins. in diameter and of the length of the inner shell was charred through and through.

In operating this model we discovered that by varying the temperatures, we could produce varying products. We also discovered that by drawing off the liquid contents of the retort after the turpentine had been distilled we could produce large quantities of an excellent grade of rosin. In fact, one of the main features of this process is its extreme flexibility.

Our commercial plant, which we have just completed and which is now in daily operation, is an exact duplicate of the model, except for the fact that the space for the bath oil is proportionately about three times as great. The large retort has an outside diameter of 5 ft., with an inner shell of 3½ ft., and a length of 28 ft. This gives us 9 ins. of oil space between the inner and outer shells.

For heating the oil bath we use a continuous coil of electrically welded pipe, containing 350 lin. ft. This pipe is set in a specially constructed furnace so that while not in direct contact with the fire, it yet gets a maximum amount of the heat. The results of this large retort have checked absolutely with the model, and we see no reason why it should not continue to do so indefinitely. I used the same oil bath in the model for 96 continuous charges, and, so far as we are able to tell, the bath oil is in exactly the condition today as when first put into service. The low cost of this oil and its long service make it an ideal menstruum for conveying the heat.

In operating this plant, we run the wood into the inner shell of the retort on cars, the doors are closed, and a steam jet is opened with leads into the inner

shell. This is done to force out the cold aid and so hasten the heating. The oil bath is then circulated from the storage tank by means of a low pressure pump through the heating coil, and so to the retort where it fills completely the space between the inner and outer shells forming a blanket of hot oil with a uniform temperature, passing out at the bottom of the retort and back to the storage tank. We control the temperature so that the inside heat shall not exceed 450° F., until we have distilled off all the turpentine and pine oil; we then allow the temperature to slowly rise until we have fractionated the light oil, and it is just at this point that destructive distillation begins and fractional distillation ceases. We find that at approximately 480° F. we begin to get the distillates with the distinctive empyreumatic odors. The temperature is held below 525° F. until all the light oil is over and then allowed to increase as fast as possible. We find that at a maximum temperature of 610° F. in the inner shell, we can get complete distillation of all the products, leaving us dry charcoal of excellent quality. At this temperature we find that our bath oil is at a temperature of 650° F., which is as high as we generally carry it, though we have gone as high as 750° F., without trouble. I do not hesitate to say that this process is the most accurate, and the apparatus the most scientific ever evolved for this work, and the results prove it.

At no stage of the process is it not under perfect control and the temperature can be raised or lowered at will. We have found by actual tests that we can hold the temperature of the oil bath at any given degree as long as may be desired. The time consumed in running a charge by this process is comparatively shorter than by any other; it takes longer than a steam process plant, but when the difference in the production is taken into account, this comparison is in our favor. We actually begin distillation as soon as the wood goes into the retort, as the oil bath is carried to about three hundred and fifty before the cars of wood are run in. After the charge is over, instead of having to wait many hours for the retort to cool, we mechanically assist the cooling by pumping cold oil through the heating chamber.

The fire risk is also a slight danger by this process, and I may say right here that an examiner for one of the leading companies in America has classed our plant as a comparatively safe risk, and is willing to write us at a very fair rate of insurance. In regard to the quantity and quality of the products produced by this method, let me say that both the turpentine and oils are of a very high grade as the samples I have with me show. The analysis of the turpentine shows it to be of remarkable quality. The production is far greater than by any other process with which I am familiar. This is best shown by the records of charges which show not only the yield but the temperature at which each product was distilled.

This daily record gives an absolutely accurate record

of the varying temperatures, both of the oil bath and the inner shell or distilling space. We also get the exact periods and temperatures at which the distillates change in nature. We may, therefore, grant that we have accomplished: first, temperature control; second, the complete utilization of the wood; third, a maximum amount of products.

This being granted, let us see what the quality is, and also consider the cost of production. In taking up the question of quality, I wish to say that it is hardly a fair comparison to consider the products made by this process against the old destructive ones, as they seem distinctly different. The turpentine as the following analysis shows is very close to the very best gum turpentine, so close, in fact, that but for one feature it would be indistinguishable; I refer now to the pine oil contents which I may say is the one means of classifying wood turpentine as against gum turpentine. The presence of this product, even in very small quantities, raises the average of the boiling points in fractionation. I believe I am correct when I say that this is the one distinction in even the very best wood turpentine. I am glad to say I am now working on a method of refining which seems to promise an easy and economical method of extracting even the slightest quantity of pine oil from refined turpentine. If this can be accomplished, I do not believe it will be possible to distinguish good wood turpentine from that distilled from the crude gum turpentines.

The following analysis of our unrefined product was made by J. E. Teeple, of New York City:

Color—slightly yellow.

Leaves no stain on paper.

Specific gravity at 16° C.—0.865.

Distillation 50 per cent at 160° C.

Distillation 80 per cent at 163° C.

Distillation 85 per cent at 164° C.

Distillation 90 per cent at 165.5° C.

Distillation 95 per cent at 172° C.

Non-volatile matter at 100° C.—0.03 per cent.

Flash-point—108.5° F.

In soluble in sulphuric acid 2.5 per cent.

Odor—Contains a noticeable odor foreign to turpentine and very similar creosate. This odor is usually removed by shaking with dilute alkali.

The turpentine is slightly acid but this acidity is easily removed by shaking with dilute alkali.

Iodine absorption No. 375.

In comparing the oils produced by this process, I cannot do better than to show samples of each of the distillates, both in crude form and as we refine them. It will be noticed that the heavy and light oils are very much brighter in color, and have a much milder odor than the ordinary destructive distillates. This is due in part to the fact that they are not burned, and are taken from the retort at their normal distilling temperatures. I have many times seen oils made by the old destructive process so black in color and so high in odor that they were hardly worth marketing,

and this was unquestionably caused by exposure to excessive temperatures. I want especially to call your attention to the samples marked "X," "XX," and "XXX" oils, also the one marked "XL." These oils are the products of special processes of refining which we have worked out, and they seem to compare very favorably with the better grades of rosin oil. They do not, however, analyze as such. We have had these oils tested out for the commercial purposes that rosin oils are used for, and they seem to serve admirably. They can be produced at much less cost.

The oil marked "XL" is worthy of notice because of the fact that it is practically odorless. In addition to this, it seems to have rather remarkable drying properties, and made into paint shows excellent wear. We have had paint samples in service for seven months or more, and the results as compared with pure linseed are very favorable indeed. Only the darker shades could be produced, however, as the oil darkens any light pigments. There is no question but that this oil will be of great value in making up a cheaper grade of paints for such purposes as freight cars and rough work generally.

In speaking of the refining of the oils produced from the distillation of pine woods, I would like to say that hardly anything has been done. I have perhaps gone as far along this line as any one, and have made, perhaps, as many as 75 distillates. I believe that this work alone offers a wonderful field for the research chemist, and it has always been a matter of wonder to me that some of our men who have the time and means to take this up, have not done so. I feel sure that no field before us today offers greater opportunities for discovery. The subject is so vast in scope that it is with great difficulty that I have been able to limit my paper to a reasonable time.

I feel that I cannot close without saying just a few words relative to the possibilities of the distillation of pine wood. There are today millions of cords of wood lying on the ground rotting, and there is a money value of approximately \$25 in each and every cord of this wood. There are every day thousands of cords of rich pine wood burned at saw-mills that have an equal money value.

The distillation of pine wood is not an industry which requires large capital. Plants may be built for comparatively small amounts that will pay good dividends. There is an unlimited demand for all the products and at prices which will pay handsomely. Many plants have failed, it is true, but every failure can be safely attributed to lack of knowledge of the industry, lack of capital or a poor process. Many men have gone into the business thinking that they could get fancy prices for the products and have been disappointed. A steady sale at a reasonable profit is all that can be expected. There is, however, a steady demand for all of the distillates now, and this demand is growing daily. The question of timber preservation has become a vital one, and when the fact that the

heavy wood oil is even more valuable than dead oil of coal tar for this purpose becomes generally known, there will be an unlimited demand for this product.

I have had offers from users of timber preservatives for very large quantities of the heavy wood oil, provided it could be furnished in sufficient quantity and at a low price. So far this has been out of the question, as one large railroad system could take all the oil made in this country. There is one feature of the industry which has done more to militate against it than anything else. I refer now to the lack of co-operation among the men engaged in the work. Every one thinks that he has a little bit more knowledge than any one else, and is jealous of it.

An association which would allow of an exchange of ideas and promote a spirit of helpfulness would do more for the art than any other one thing. Trade secrets need not be divulged, but matters of moment for the good of all could be promoted by such an organization, and only by such.

TYPICAL EXPERIMENTAL TESTS.

Charge No. 19—April 25, 1911.

20 lbs. wood (good).

Inside. Outside.

7:30 a. m.	Fire started.		
8:30 a. m.	Turps. started.....	380°	510°
9:00 a. m.		395	477
10:00 a. m.		413	480
11:00 a. m.		451	556
12:00 m.		484	567
1:00 p. m.	Turps. stopped.		
	Light oil started.....	494	578
2:00 p. m.		508	590
3:00 p. m.	Light oil stopped.		
	Heavy oil started.....	572	675
4:15 p. m.		581	666
5:00 p. m.		597	690
6:00 p. m.		595	675

Calculated to Cord Basis.

Charcoal	30	bushels.
Residue	20	gals.
Crude turps.	50.0	gals.
Crude light oil.....	15.23	gals.
Crude heavy oil.....	78.12	gals.

143.35 gals.

Charge No. 26—May 3, 1911.

20 lbs. wood.

Inside. Outside.

7:40 a. m.	Fire started.		
8:40 a. m.	Turps. started	380°	510°
9:00 a. m.		387	507
10:00 a. m.		420	510
11:00 a. m.		428	522
12:00 m.		467	565
1:00 p. m.	Turps stopped.		
	Light oil started.....	490	578
2:00 p. m.	Light oil stopped.		
	Heavy oil started.....	536	641
3:00 p. m.		570	678
4:00 p. m.		596	678
5:00 p. m.		594	674
5:30 p. m.		592	680

Calculated to Cord Basis.

Charcoal	25	bushels.
Residue	30	gals.
Crude turps.	38.06	gals.
Crude light oil	10.15	gals.
Crude heavy oil	106.25	gals.

154.46 gals.

Charge No. 11—April 15, 1911.

20 lbs. wood (good).

Inside. Outside.

9:30 a. m.	Fire started.		
10:00 a. m.		270°	430°
10:30 a. m.	Spirits started	345	525

11:00 a. m.		374	489
12:00 m.		378	436
1:00 p. m.		384	435
2:00 p. m.		385	430
3:00 p. m.		392	432
3:25 p. m.	Rosin started	387	416
3:55 p. m.	Rosin stopped	395	455
4:00 p. m.		408	508
5:00 p. m.		520	615
5:10 p. m.	Stop fire	528	628

24 ozs.
spirits.
(Rosin
2½ lbs.)

Calculated to Cord Basis.

7 ozs. light oil on cooling down:	
Wood left	12.0 lbs.
Residue	4.0 ozs.
Crude turps.	37.44 gals.
Crude light oil	
Rosin	500.0 lbs.

Charge No. 15—April 20, 1911.

20 lbs. wood (good).

Inside. Outside.

8:10 a. m.	Fire started.		
9:00 a. m.	Spirits started	372°	500°
10:00 a. m.		408	484
11:30 a. m.		435	535
12:00 m.		452	550
1:00 p. m.		500	600
1:15 p. m.	Spirits stopped.		
	Light oil started.....	508	623
2:00 p. m.		540	650
2:20 p. m.	Light oil stopped.		
	Heavy oil started.....	550	662
3:00 p. m.		574	677
4:00 p. m.		595	680
5:00 p. m.		607	692
5:25 p. m.		605	690

24½ ozs.
spirits.
7½ ozs.
light oil.
60 ozs.
heavy oil.

Calculated to Cord Basis.

Charcoal	28	bushels.
Residue	20	gals.
Crude turps.	38.2	gals.
Crude light oil.....	11.7	gals.
Crude heavy oil.....	93.6	gals.

Charge No. 35—May 13, 1911.

20 lbs. wood.

Inside. Outside.

7:30 a. m.	Fire started.		
8:45 a. m.	Turps. started	344°	459°
9:00 a. m.		363	473
10:00 a. m.		405	490
11:00 a. m.		415	483
12:00 m.		465	560
12:45 p. m.		502	598
1:00 p. m.		508	602
2:00 p. m.		535	620
3:00 p. m.		575	661
4:00 p. m.		610	670
5:00 p. m.		608	660
5:30 p. m.		600	650

19½ ozs.
turps.
6 ozs.
light oil.
67 ozs.
heavy oil.

Calculated to Cord Basis.

Charcoal	28	bushels.
Residue	20	gals.
Crude turps.	30.46	gals.
Crude light oil.....	9.37	gals.
Crude heavy oil.....	104.68	gals.

Charge No. 40—May 19, 1911.

20 lbs. wood.

Inside. Outside.

7:15 a. m.	Fire started.		
8:30 a. m.	Turps. started	376°	485°
9:30 a. m.		430	520
10:30 a. m.		465	526
11:30 a. m.		476	544
12:30 p. m.		485	541
1:30 p. m.		512	583
2:30 p. m.		550	640
3:00 p. m.		580	672
4:00 p. m.		596	675
5:00 p. m.		612	674
5:30 p. m.		610	670

20½ ozs.
turps.
10 ozs.
light oil.
67 ozs.
heavy oil.

Calculated to Cord Basis.

Charcoal	28	bushels.
Residue	15	gals.
Crude light oil.....	15.62	gals.
Crude turps.	32.03	gals.
Crude heavy oil.....	104.68	gals.

Charge No. 47—May 27, 1911.

20 lbs. wood.

Inside. Outside.

7:00 a. m.	Fire started.		
8:15 a. m.	Turps. started	400°	480°
9:00 a. m.		429	508
10:00 a. m.		460	525
11:00 a. m.		492	565
12:00 m.		502	596
1:00 p. m.		545	622
2:00 p. m.		562	642
3:00 p. m.		573	637
4:00 p. m.		605	685
5:00 p. m.		600	676

Calculated to Cord Basis.

Charcoal	28	bushels.
Residue drawn off	40	gals.
Crude turps.	42.96	gals.
Crude light oil	8.59	gals.
Crude heavy oil	97.65	gals.

Charge No. 50—May 31, 1911.

20 lbs. wood.

Inside. Outside.

7:00 a. m.	Fire started.		
8:05 a. m.	Turps. started	388°	508°
9:00 a. m.		425	520
10:00 a. m.		455	540
11:00 a. m.		481	571
12:00 m.		501	583
12:20 p. m.		515	600
1:00 p. m.		532	611
1:30 p. m.		543	643
2:00 p. m.		572	655
3:00 p. m.		610	684
3:30 p. m.		614	675

Calculated to Cord Basis.

Charcoal	30	bushels.
Residue drawn off	20	gals.
Crude turps.	50.00	gals.
Crude light oil	10.93	gals.
Crude heavy oil	101.56	gals.

Charge No. 58—June 9, 1911.

20 lbs. wood.

Inside. Outside.

8:10 a. m.	Fire started.		
9:20 a. m.	Turps started	374°	500°
10:00 a. m.		436	543
11:00 a. m.		476	566
12:00 m.		517	607
12:30 p. m.		526	617
1:00 p. m.		540	632
1:30 p. m.		552	641
2:00 p. m.		563	648
3:00 p. m.		600	677
4:00 p. m.		608	680
4:30 p. m.		600	670

Calculated to Cord Basis.

Charcoal	28	bushels.
Residue drawn off	20	gals.
Crude turps.	36.71	gals.
Crude light oil	10.93	gals.
Crude heavy oil	103.12	gals.

Charge No. 79—July 5, 1911.

20 lbs. wood.

Inside. Outside.

7:30 a. m.	Fire started.		
8:36 a. m.	Turps. started	385°	508°
9:00 a. m.		411	522
10:00 a. m.		449	536
11:00 a. m.		474	556
11:55 a. m.		497	591
12:57 p. m.		546	636
2:00 p. m.		590	677
3:00 p. m.		598	681
3:35 p. m.		600	682

Calculated to Cord Basis.

Charcoal	4½	lbs.
Residue	2½	lbs.
Crude turps.	44.53	gals.
Crude light oil	11.54	gals.
Crude heavy oil	112.50	gals.

Charge No. 82—July 10, 1911.

20 lbs. wood.

Inside. Outside.

7:10 a. m.	Fire started.		
8:20 a. m.	Turps. started	384°	495°
9:00 a. m.		409	512

10:00 a. m.	448	551	29 ozs. water.
11:00 a. m.	477	560	
11:40 a. m.	498	593	9 ozs. light oil.
1:00 p. m.	542	630	10½ ozs. water.
1:10 p. m.	546	631	
2:00 p. m.	575	667	50 ozs. heavy oil.
3:00 p. m.	584	661	26 ozs. water.
4:00 p. m.	579	644	

Calculated to Cord Basis.

Charcoal	30	bushels.
Residue	35	gals.
Crude turps.	51.56	gals.
Crude light oil	14.06	gals.
Crude heavy oil	78.12	gals.

Charge No. 90—Aug. 12, 1911.

20 lbs. Western wood.

Inside. Outside.

8:25 a. m.	Fire started.		
10:08 a. m.	Turps. started	397°	473°
11:00 a. m.		414	477
12:00 m.		439	495
1:00 p. m.		459	511
2:00 p. m.		486	562
3:00 p. m.		551	622
4:00 p. m.		606	702
5:00 p. m.		637	682
5:30 p. m.		631	686

Refined Products.

W. W. turpentine	40.0	Gals.
Secord turpentine	1.5	
Light oil	10.5	
Light product, No. 1	3.1	
Light product, No. 2	2.7	
Heavy oil	87.5	
Refined to extra heavy oil	40.6	

185.9

Calculated to Cord Basis.

Charcoal	950 lbs.	4¾ lbs.
Residue	138 lbs.	11 ozs.
		Gals.
Crude turps.		50.39
Crude light oil		15.62
Crude heavy oil		140.62

TESTS ON COMMERCIAL PLANT.

Charge No. 1—March 19, 1912.

4,653 lbs. wood. Temperature.

Time.	Changes.	Retort.	Oil.	Output.
5:15 a. m.	Pumps started			
6:30 a. m.	Steam turned in retort			
6:43 a. m.		226°		
8:00 a. m.	Oil turned in retort below	260		
8:00 a. m.		217		
8:17 a. m.	Steam cut off	217		
9:15 a. m.		218		
10:07 a. m.		225	272°	33 gals. turps.
10:15 a. m.	Cut out tank			
11:05 a. m.		255	315	
12:00 m.		276	345	
1:00 p. m.		309	393	
2:00 p. m.		332	440	
3:00 p. m.		366	477	
4:00 p. m.		380	520	
5:00 p. m.		425	549	
5:20 p. m.		445	559	
6:12 p. m.		480	587	
6:30 p. m.		486	596	20 gals. light oil.
8:34 p. m.		502	603	
9:35 p. m.		550	631	
10:33 p. m.		563	646	
11:34 p. m.		575	649	
12:33 a. m.		562	646	86 gals. heavy oil.
1:35 a. m.		558	643	
2:22 a. m.		559	643	
3:30 a. m.		555	645	
3:55 a. m.		557	645	

Charge No. 2—March 21, 1912.

1-cord slabs—5,076 lbs.

Temperature.

Time.	Changes.	Retort.	Oil.	Output.
6:50 a. m.	Oil and steam on.			
7:10 a. m.	Steam cut off	210°		
8:00 a. m.		181	259°	
9:00 a. m.		191	272	
10:00 a. m.		226	326	
11:00 a. m.		262	356	

11:43 a. m.	Dist. started	286	377	
12:00 m.		283	384	
1:17 p. m.		290	415	
2:00 p. m.		300	423	
3:00 p. m.		285	430	
4:05 p. m.		296	442	
5:05 p. m.		300	455	
6:00 p. m.		325	467	33 gals. crude turps.
7:00 p. m.		377	478	
8:00 p. m.		389	488	
9:00 p. m.		402	495	
10:00 p. m.		405	500	
11:00 p. m.		411	500	
12:03 a. m.		415	507	
1:00 a. m.		422	511	
2:00 a. m.		431	516	
3:00 a. m.		437	527	
4:00 a. m.		448	535	
4:35 a. m.	Dist. changed	457	541	
5:00 a. m.		465	542	
6:00 a. m.		480	555	10 gals. light oil
7:00 a. m.	Dist. changed	498	563	
8:00 a. m.		502	568	
9:00 a. m.		504	576	
10:00 a. m.		504	587	79.29 gals. heavy oil
11:00 a. m.		512	599	
12:00 m.		504	604	
12:45 p. m.	Charge stopped, leaky pipe			
	47.21 gals. pitch.			

Charge No. 3—March 25, 1912.

1-cord slabs—4,508 lbs.

Temperature.

Time.	Changes.	Retort.	Oil.	Output.
6:30 a. m.	Steam on for 3 min.			
6:33 a. m.	Oil started in retort.	218°	300°	
7:00 a. m.		175	295	
8:00 a. m.		218	318	
9:00 a. m.		240	347	
10:00 a. m.		268	368	
10:30 a. m.	Dist. started	294	377	
11:00 a. m.		306	382	26 gals. crude turps.
12:00 m.		321	400	
1:00 p. m.		335	427	
2:00 p. m.		348	455	
3:00 p. m.		394	477	
4:00 p. m.		409	492	
5:00 p. m.		428	513	
6:00 p. m.		451	532	
7:00 p. m.		469	543	
8:00 p. m.		483	561	7½ gals. crude light oil
9:00 p. m.	Dist. changed	500	570	
10:05 p. m.		525	589	
10:30 p. m.	Dist. changed	533	595	
11:00 p. m.		540	606	
12:00 m.		549	616	44 gals. heavy oil
1:00 p. m.		556	627	
2:30 p. m.		559	648	
	42.38 gals. pitch.			

The U. S. Geological Survey has just issued an advance statement of the production of copper in 1911. This statement, prepared by B. S. Butler, gives the final figures of production as made up from reports from all the reduction plants. The preliminary estimate of the smelter output of the country, issued by the Geological Survey January 2, 1912, differed from the final figures by but a fraction of 1 per cent. The total smelter production from ores mined in the United States was 1,097,232,749 lbs. This is the largest production in the history of the industry and compares favorably with the output of 1,080,159,509 pounds for 1910. Arizona again heads the list of copper producing states, with a production of 303,202,532 lbs., the largest production ever made by the state. Montana is second, with 271,814,491 lbs., Michigan third, with 218,185,236 lbs.; and Utah, fourth, with 142,340,215 lbs.

NATURAL GAS INVESTIGATIONS OF THE BUREAU OF MINES.*

By GEORGE A. BURRELL.

Last year at the Pittsburgh convention of the Natural Gas Association, a resolution was passed, asking that the Bureau of Mines assist the natural gas industry in solving problems which arise in the utilization and conservation of natural gas. Although not as active in its investigations as it hopes to be in the future, some progress has been made toward a study of this important fuel.

No attempt has as yet been made toward a complete comparative study of the natural gases from different fields of the country. Some work has been accomplished in that the characteristics of the gas from a few wells in some of the more important fields have been determined, but the bureau is gathering from many wells in all of the fields a large number of samples, and is submitting them to examination. A bulletin covering this work will be ready for distribution the latter part of the present year. Work already accomplished makes it appear that natural gas consists of paraffin hydrocarbons with nitrogen and carbon dioxide as impurities. The paraffin hydrocarbons may be methane only, or a mixture in which methane and ethane predominate with smaller percentages of the higher paraffin hydrocarbons, or in the case of rich casing head gases, a mixture in which ethane and propane predominate. The carbon dioxide may range from a trace as in the case of the gases of Western Pennsylvania, to as much as 30 per cent as found in a sample of natural gas obtained from Kings County in Southern California. Nitrogen may occur in quantities ranging from a few tenths of 1 per cent to as much as 10 or 15 per cent. As an example of an unusual and extreme case, the bureau found that a natural gas occurring in the state of Washington contained 98 per cent of nitrogen. In general it may be said that those gases issuing under considerable pressure in the great fields which are providing heat and light for many towns consist of paraffin hydrocarbons in which methane predominates along with smaller quantities of ethane and traces of the still higher paraffins. These gases range in heating value from 900 to 1,100 B. t. u. per cubic foot at 0° C. and 76° Mm. pressure with the average more nearly approaching the latter figure. In these days when the heating value is the important factor in determining the usefulness of a gas, such high values are very significant. Contrary to usual text-book information, the bureau has not been able to detect in those gases examined, the presence of olefine hydrocarbons, carbon monoxide and hydrogen, although exhaustive tests have been made for these constituents. Natural gases do not well lend themselves to the ordinary examination to which gases are usually submitted. These points will be emphasized

*Presented at the 7th annual convention of the Natural Gas Association of America, Kansas City, Mo., May 21-22-23, by permission from the Director of the Bureau of Mines.

in the forthcoming report. It is believed that an analyses of natural gas which shows carbon monoxide, hydrogen and olefine hydrocarbons should be carefully looked into regarding the method employed in its examination. The composition of the gas has an important bearing, viewed from several standpoints.

First let it be emphasized that we have in natural gas, a fuel rich in heat units, non-poisonous, diminishing in quantity and which can only be replaced as nature sees fit, selling for less than a manufactured product, which is not its equal.

From the composition can be determined the relative value of the different gases. It appears that the composition of the gas from a particular well does not vary materially over long periods of time, so that once fixed, one need not expect to find in the future a gas from the same well which will have changed materially in composition. Sufficient data is not at hand to make this a sweeping statement covering all cases. But in the case of the natural gas supplied to Pittsburgh, the bureau finds that its composition does not vary appreciably from its composition as determined by F. C. Phillips about eighteen years ago. This gas comes from many different wells in the Appalachian fields.

Not infrequently, a warning is raised against the introduction of too much carbon monoxide into illuminating gas. Carbon monoxide gives to coal and water gas their deadly powers of asphyxiation, and where the content is high, the intrusion of the gas into a room from a defective connection may result fatally, when we consider that as little as .2 or .3 per cent of CO in a room, after a sufficient lapse of time, will bring about unconsciousness and death. Such being the case we are extremely fortunate that natural gas does not contain carbon monoxide.

No one doubts the great importance of the correct determination of the genesis of natural gas and petroleum. Probably the prevailing opinion of the present day has it that natural hydrocarbons are of organic origin, although sufficient proof is not at hand to say that at least some of them may not be of inorganic origin. If of inorganic origin, say by the action of superheated water on the carbides of iron, according to Mendeleif's hypothesis, then we may be justified in believing that natural gases should contain those constituents that are produced by the decomposition of carbides when the experiments are performed in the laboratory. We could still go farther and believe that the formation of natural gas is continuously taking place, for we are not justified in saying that the carbides have long since been exhausted. Mendeleif's theory, however, does not stand up in the face of these chemical considerations. The theory that natural hydrocarbons are produced by the destructive distillation of either animal or vegetable matter receives the most support. If such is the case, oil and gas become stored products and are not being continuously generated at the present time. It will be seen from this brief summary that an accurate knowledge of the

composition of the different gases becomes essential in order to throw all possible light on the elucidation of the genesis of natural gas. "Where can gas be found?" is the insistent demand of those who already feel the pinch of a diminishing supply. Geologists are in possession of certain facts that help to diminish the risk in drilling wells, but it is only when the drill has made the boring that doubt becomes removed.

Little need be said here about the production of gasoline from natural gas. Suffice to say that by this means a highly useful fuel is being obtained for which there is an ever increasing demand. The industry rapidly developed from its swaddling clothes so that now it threatens to add considerably to the total quantity of gasoline produced. All natural gases, of course, are not adapted to the manufacture of gasoline. A few wells produce methane as the only hydrocarbon, and for the liquefaction of methane, a pressure of 50 atmospheres at 94° C. is required. Some gases, as Pittsburgh natural gas, some of your Oklahoma gases, and many others contain a large proportion of methane, a smaller proportion of ethane and not near enough of the higher paraffin hydrocarbons for the commercial production of gasoline. Other gases, casing head gases, and those drawn from the earth under reduced pressure, may be so rich in the higher paraffin hydrocarbons, butane, pentane, hexane, etc., that five or more gallons of gasoline per 1,000 cubic feet of gas may be extracted. A chemical examination will show what may be expected from a particular gas in the way of gasoline production with a given plant equipment. The bureau is making a study of these methods of examination. Perhaps the simplest of the tests applied at the present time consists in shaking the gas with some solvent such as olive oil, cotton seed oil, clairolene oil, etc., in which the higher paraffin hydrocarbons are more soluble than the lower. It was found for instance, that by shaking 100 c. c. of a gas from which a very high yield of gasoline is obtained in 35 c. c. of clairolene oil that 80 per cent of the gas dissolved in the oil. Pittsburgh natural gas lost only 15 per cent of its volume when treated in the same way. The latter gas cannot be used for the commercial production of gasoline.

The bureau has issued one publication having to do with the properties of liquefied natural gas. In the production of gasoline a very great waste has occurred, because in order to make condensates safe for shipment, the lighter products have been allowed to evaporate. The confinement of the material in iron cylinders for use as a bottled gas is now receiving attention. A gas is produced which has a heating value of at least 2,200 B. t. u. per cubic foot, and a candle power of about 45 when burned as a naked flame at the rate of 5 cubic feet per hour. The use of a mantle will, of course, increase this lighting effect greatly. In order to bring this means of utilizing natural gas to your attention, Mr. I. C. Allen and the writer simply bottled in strong cylinders the condensate obtained by

applying a pressure of about 500 lbs. to the square inch and a temperature of 0° C. to crude gas obtained from wells at Follansbee, W. Va. There are some here who could do the same with their casing head gas, which is at present going to waste. Once bottled it is only necessary to slightly crack the valve to obtain a supply of true gas.

In experiments conducted at the bureau, the gas was passed through a small meter, and then burned in a Junker Calorimeter. Samples of the gas were also analyzed. By taking the gas from the bottom of the tank its composition remained uniform throughout the test. In the case of the exceedingly rich gas obtained at Follansbee, W. Va., about 50 cu. ft. of gas per gallon of liquid was realized. For the better control of the gas as it issued from the bottle, a reducing valve was attached.

The bureau has, of course, viewed this manner of utilizing natural gas from the standpoint of a purely technical investigation, with no axe to grind, except a step in the conservation of natural resources and believes that some of the gas at present going to waste will eventually be used this way. Millions of people are so situated that gas is not used by them, but if a bottled gas sold at a reasonable price becomes available, the outlet for the material will be large. The bureau has recently learned that one company is already in the field for the purpose of exploiting the liquid gas. They have named their product "Gasol."

Another means of utilizing natural gas has been tried in that attempts have been made to prepare substitution products, principally chloroform, by the action of chlorine upon methane. Although seemingly difficult to do commercially, one cannot say that such will always be the case. Mention is simply made of this process as showing that the entire utilization of natural gas may not always be along the line of combustion processes.

Probably in but few instances has surface combustion been applied in this country as yet to the use of natural gas. The Yankee seems to want to discount Prof. Bone's figure of a 92 per cent efficiency in the case of gas fired boilers and make it about 88 per cent, but even so this is a noteworthy advance and opens up a wide field for the saving of gas in combustion processes. An installation is not complicated or costly.

In the every day use of natural gas for domestic purposes, saving may be accomplished if appliances are used which are best suited to the economical combustion of natural gas. Natural gas burners require more air than coal gas burners, and if the same burner regulation is used for natural gas that works well with coal gas, then the former is not being completely burned. Some natural gas appliances in use are notoriously inefficient. Progressive gas men should give this question of proper appliances serious consideration.

Natural gas is cheap and the tendency may be to use more for any particular purpose than is necessary. A

campaign along this line which would result in a smaller consumption of gas per family, should help remove some of the objection to the inevitable rate rise.

In conclusion it can be stated that the Bureau of Mines wants to do all it can to conserve the natural gas supplies. Great care must be exercised in the use of deposits which are only bubbles and which when punctured become exhausted. Reckless waste of the gas in the field should be prevented by legislation, and every effort should be made toward the education of all concerned that they may realize the necessity of conserving the supply. It is believed that the Bureau of Mines can do more efficient work along the latter line.

LOSSES OF COMBINED NITROGEN.*

By JOHN D. PENNOCK.

Before taking up the consideration of the losses of combined nitrogen in organic substances, to which this discussion will be chiefly confined, it may be well to devote a few words to the loss of nitrogen (1) combined in inorganic substances, and (2) the loss of nitrogen in the gaseous form freed from the oxygen of the air.

Of course, the chief source of inorganic nitrogen combined in mineral form as a natural deposit is Chile saltpeter, or nitrate of soda, formed chiefly on the western coast of South America in the province of Tarapaca, Chile.

Because of the naturally restricted confines of this mineral and the comparatively small quantity known to exist (variously estimated, at the existing rate of consumption, to supply the world's demand for 50-75 years), its conservation in every way possible is a matter of exceedingly great importance.

Now, the losses of this mineral, containing 16.4 per cent nitrogen, which is so important to agriculture as well as the arts, may come about (1) in the mining and refining of the impure mineral, called "Caliche," and (2) in the utilization of the refined product.

The "Caliche" (brown) found in the province of Tarapaca is shown by analysis¹ to be of the following composition:

	Per cent.
Sodium nitrate.....	60.97
Sodium iodide.....	0.73
Sodium chloride.....	16.85
Sodium sulphate.....	4.56
Calcium sulphate.....	1.33
Magnesium sulphate.....	5.88
Insoluble	4.06
Water	5.64

While as seen above the product as mined in Tarapaca is comparatively rich in nitrate of soda, that mined in the provinces of Pampa de Tamorugal and Atacama contains from 25 per cent to 50 per cent NaNO_3 .

It is likely that in the process of refining this Caliche, which consists in lixiviating, settling or filtering, evaporation and crystallization, there is a considerable loss

*From the Journal of Industrial and Engineering Chemistry
¹Machalske, Am. Fertilizer, 25, 8.

of the valuable NaNO_3 . Just what this loss amounts to, the very meagre scientific information available does not enlighten us.

These deposits of nitrate are of vital importance to the world at large and, though they are held by private corporations, principally German, the Chilian government having been forced to retire from the business because of the competition of the private operators, they should be carefully conserved. Further, it might be desirable that an international committee, composed of chemists appointed by the governments of those countries most vitally interested, should visit the nitrate fields, determine what losses exist, if any, study into the present methods of refining the crude product and make recommendations for the improvement of these methods, if found unsatisfactory.

It is difficult to determine how economically the 2,251,000 tons of nitrate of soda shipped from Chile in 1910 was used. Of this, during 1910, 535,820 tons came to the United States and was used in the arts as follows:

	Per cent.
In manufacture of fertilizers.....	13
In manufacture of dyestuffs.....	12
In general chemistry.....	10
In glass.....	4
In explosives.....	41
In nitric acid.....	9
In sulphuric acid.....	6
Unaccounted for.....	5

Most of the nitrate used in dyestuffs and explosives passes through the form of nitric acid. In the manufacture of nitric acid by the ordinary method, 90-93 per cent of the nitrogen of the nitrate is converted into nitric acid; the yield may be increased and the loss of combined nitrogen from this source reduced by the use of the Valentina vacuum process which will bring the yield to 97-98 per cent.

PURE NITROGEN.

In the early days of the manufacture of calcium cyanamide, the nitrogen necessary for the treatment of the carbide was obtained by separating nitrogen from liquid air; later the oxygen of the air was removed by passing the air over heated copper, the oxide being subsequently reduced by heating with natural gas (at Niagara Falls).

The waste gases of the precipitating towers of an ammonia soda process furnishes an abundant (2,940 tons per day in this country) supply of nitrogen which would be suitable for the manufacture of cyanamide. The oxygen of the air used to burn the coke in the lime kilns is completely converted to CO_2 , so that the gas going to the precipitating towers contains only CO_2 and N, when leaving the tower is practically pure nitrogen, there being one to two per cent of CO_2 which could be readily absorbed by passing the gas through milk of lime: A cyanamide plant, however, is preferably located where there is cheaper power and hence cannot utilize the cheap nitrogen from an ammonia soda works.

LOSSES OF THE COMBINED NITROGEN IN ORGANIC SUBSTANCES.

The losses of the nitrogen contained in inorganic substances is unimportant compared with the losses which daily occur to the extent of hundreds of tons from the improper use of the organic substances which contain it. Further, there are many organic substances containing such high percentages of nitrogen, which at present go to waste or lie in the earth unutilized, which would produce so high a yield of ammonia that the dry distillation for ammonia alone would be very profitable. Among these substances may be mentioned shale, peat, garbage after the removal of the oils and fats, and sewage sludge. These products will yield on distillation 75-85 lbs. of ammonium sulphate per ton, or 3 times as much as coal.

Of all the losses of combined nitrogen, that which goes to waste in the manufacture of coke by the beehive process is the greatest.

In the conferences on the conservation of mineral resources inaugurated by ex-President Roosevelt a few years ago, the great loss of fuel² and valuable nitrogen in the beehive method of coke-making occupied a prominent part in the discussions.

James Douglas,³ in a paper on "Conservation of Natural Resources," deplored the loss of coal and valuable by-products but stated that the development of by-product ovens could not rapidly proceed to displace the beehive ovens because chemical industry was unable to assimilate and utilize the by-products with suitable returns.

Since 1893, when the first by-product coke oven was built at Syracuse, and it was demonstrated that retort coke was equal in quality to that made in the beehive oven and the by-products, tar, ammonia, benzole and cyanides, could be recovered in sufficient quantity to make the operation a profitable one, there has been no justification for the construction of additional beehive ovens.

It is perhaps true that that particular chemical industry which converts benzile and other coal tar products into colors and refined chemicals is pretty effectually fixed in the hands of Germans and not easily wrested from them, and they may continue to ship to this country seven million dollars worth of colors, but the consumption of sulphate of ammonia for fertilizers is increasing at such a rate that the United States production cannot supply the demand and nearly as much is imported as is made in this country. Further, the price is higher than it has been for several years. The same may be said of the price of tar. New uses for tar have been found so that the price has not fallen appreciably in the last ten years, although the production has increased enormously.

To what extent losses of combined nitrogen have occurred since 1893, when the retort coke ovens were

²The easily accessible coals will be exhausted about the year 2027. M. R. Campbell and E. W. Parker, Am. Inst. Min. Eng., 40, 258.

³Am. Inst. Min. Eng., 40, 419.

introduced and the loss could have been avoided, a glance at the coke statistics will show. From 1893-1910 inclusive the coal coked in beehive ovens, where the volatile nitrogen was ruthlessly wasted in fire, amounted to about 810,000,000 tons. Had this been coked in by-product ovens, the volatile nitrogen of the coal would have yielded 23 lbs. of ammonium sulphate per ton, or a total of 9,315,000 tons, which at \$60 per ton would have had a value of \$558,900,000. But this would not be all. Had this ammonia been recovered, it would have been used on the soil as a fertilizer, the crops would have been increased fully 20 per cent and the saving would have been many millions more.

PERCENTAGE OF PURE NITROGEN EVOLVED AND RECOVERED.

In the various Semet-Solvay plants throughout this country the nitrogen content of the coals varies from 1.2-1.46 per cent. The evolved nitrogen amounts to about 33 per cent of the total contained in the coal.

Taking the results of the distillation at one of these plants, we have the distribution of the nitrogen as follows: [The nitrogen in all cases is figured to $(\text{NH}_4)_2\text{SO}_4$].

	Lbs. $(\text{NH}_4)_2\text{SO}_4$ per ton coal.
Coal, 1.3 per cent nitrogen figured to sulphate.....	122.6
Ammonia yield, actual sulphate.....	25.0
Nitrogen left in coke, as sulphate.....	78.2
Nitrogen left in 10,000 cu. ft. gas as sulphate..	12.0
Nitrogen in tar (90 lbs. per ton) as sulphate..	3.5
Nitrogen in pyridine.....	0.3
Nitrogen in cyanides.....	0.4
Unaccounted for.....	3.2

Thus the nitrogen in the coal is distributed in the various forms, as follows:

	Per cent.
Recovered as ammonia.....	20.3
Remaining in the coke.....	63.7
As elementary nitrogen in gas.....	8.1
In tar.....	2.9
As pyridine.....	0.25
As cyanide.....	0.3

Attempts have been made to increase the amount of nitrogen converted to ammonia. In cases where the ash of the coal is low, it is permissible to add lime, which must be very intimately mixed in a state of powder. The ammonia yield is increased from 10-15 per cent. If the walls of the ovens are laid up with silica brick, the lime in the coal is likely to flux with the brick and the coke will stick to the walls.

The result of a trial for five months⁴ of adding 2 per cent lime to coal carbonized in a gas works at Cheltenham, England, was an increase of 1.88 lbs. sulphate of ammonia per ton. There was an additional advantage of reducing the sulphur in the gas from 40-21.5 grains per 100 cubic ft.

METALLIC OXIDES REDUCE AMMONIA YIELD.

At one of the plants located near a blast furnace which received its supply of coke from the by-product ovens, the fine iron oxide flue dust was mixed with the coal being charged to the ovens, thinking thus to save it from the dump heap, but the effect of a 3 per cent of oxide introduced caused the NH_3 yield to fall off 8 per cent.

OTHER WAYS OF SAVING NITROGEN OF COAL.

Hundreds of thousands of tons of coal per annum are converted into producer gas in the Mond producers in England, steam being used to blow the producers and to maintain a low temperature. The gases are washed with acid and 80 lbs. of ammonium sulphate are obtained per ton of coal, four times as much as would be obtained from the same coal in a retort coke oven.

The ultimate solution of the problem of the utilization of peat will probably be the conversion to gas in a producer and the utilization of this gas in gas engines, for the handsome return from the 110 lbs. $(\text{NH}_4)_2\text{SO}_4$ saved per ton will make the proposition very profitable.

On account of the high percentage of oxygen in peat, dry distillation destroys the ammonia, but in the Mond producer, peat containing 50 per cent moisture may be gasified, showing 75-80 per cent⁵ conversion of the nitrogen of the peat to ammonia: 4,000 cubic m. of gas of 1,400 calories are obtained from one ton of peat and 3-6 per cent tar containing 15 per cent of soft paraffin and 50 per cent neutral oils suitable for Diesel motors.

That there is some progress toward substitution of by-product ovens for beehive is shown by the following figures: In 1900 there was total coal coked, 20,533,348 tons. In that year 1,075,727 tons were coked in by-product ovens, or 5 per cent of the total. In 1910, of the total coke made, 41,708,810 tons, 7,138,734 tons were made in by-product ovens, or 17 per cent. This advance is encouraging. What is more encouraging is the fact that the government statistics show that a smaller number of beehive ovens were being built in 1910 than previous years and that of the total ovens, 2,567 building at the end of 1910, 1,200, or 46.75 per cent, were by-product ovens. As the average coking capacity of a by-product oven is four times that of a beehive, it is evident that the additional producing capacity of 1910 was more largely by-product than beehive.

COMPARATIVE ADVANCEMENT IN SAVING OF COMBINED NITROGEN IN GERMANY, ENGLAND AND THE UNITED STATES.

When Germany began to develop the coal tar color industry she was forced to import her tar from England; the necessity for increasing the supply of tar caused Germany at once to begin abandoning the beehive ovens, substituting retort coke ovens. In 1900, 30 per cent of the coke made in Germany was coked in retort ovens. In 1910, so complete had the transformation to retort ovens taken place that over 80 per cent was made with recovery of ammonia and other by-products. Soon all the coal used for coke-making in Germany will be coked with the recovery of by-products. When this time arrives the retort oven will be operated for tar and ammonia as primary products and coke secondary. At such time ammonia from cyanamide or synthetic ammonia will be produced in

⁴J. Soc. Chem. Ind., 30, 288, 1367.

⁵Chemiker Zeitung, May 11, 1911, p. 505.

large quantities as higher prices will make these processes profitable.

England until 1910 has been the greatest producer of sulphate of ammonia. In this year Germany nearly equaled England's production. In 1900, 10 per cent of England's metallurgical coke was made in retort ovens; in 1910, over 18 per cent was so made.

The retort coke output in the United States in 1900 was 5 per cent of the total. In 1910 this had increased to 17 per cent.

Chart I. shows the increase in retort coke output year by year.

The relative standing of the four greatest producers of ammonia in the world is shown in Chart II.

Imports, domestic production, and price of ammonium sulphate are given in Chart III.

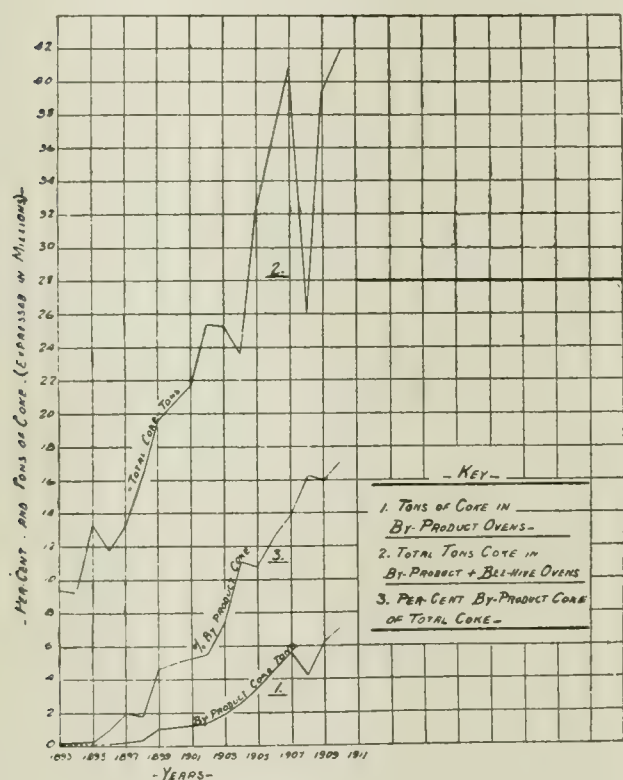


Chart I.

A steel manufacturer considering the expansion of his iron and steel business runs against these facts in considering by-product ovens: A beehive oven costs about \$400 and cokes 2.2 tons of coke a day; a by-product oven cokes 10 tons a day and costs, including by-product apparatus and all equipment for entire operation, \$11,000-\$12,000; but in spite of the greater capital invested, he can get his coke at his furnace at the same time and pay interest and depreciation on the larger investment, because of the value of the by-products obtained.

It may be shown that a corporation owning its Connellsville coal lands, and its beehive coke ovens at Connellsville, and blast furnaces and steel mills at Pittsburgh, can well afford to shut down its beehive ovens and make its coke in by-product ovens at Pittsburgh from coal shipped from Connellsville. The corpora-

tion would get its coke at the same price, taking into consideration the increased yield of coke in by-product ovens, and reducing the gross cost of the coke by the returns from tar, benzole, and part of the ammonia. In addition to supplying the coke at the same price,

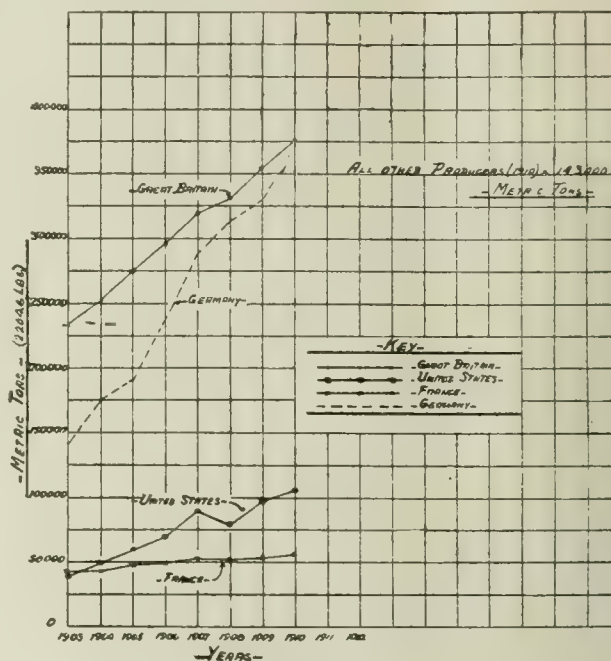


Chart II.

there will be a large part of the ammonia yield which would not be required as a credit to bring the price of the by-product coke down to the price of the beehive at Connellsville plus freight to Pittsburgh. The extra amount of ammonia is then a by-product which has cost absolutely nothing.

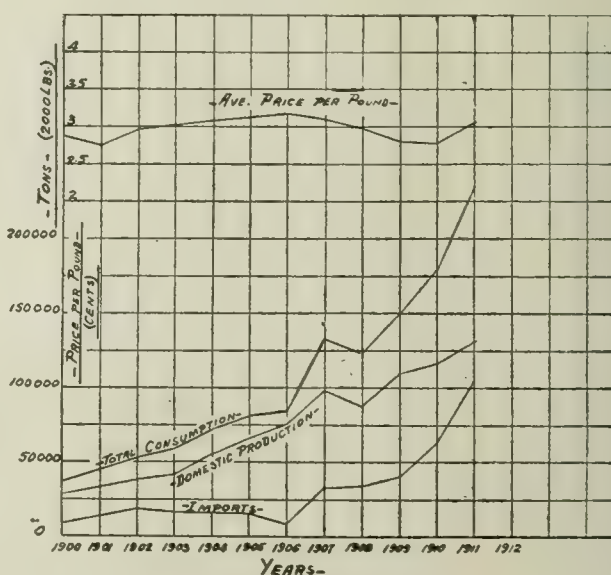


Chart III.

An important factor in reducing the cost of by-product coke is the much higher yield obtained, as stated above. The yield of Connellsville coke in by-product ovens is 73 per cent, while in beehive ovens it is 66 per cent, or 10.6 per cent greater. Assuming this rate of increase in yield for all coal coked in bee-

COMPLETE LIST OF BY-PRODUCT AND RETORT COKE-OVEN PLANTS IN THE UNITED STATES, JANUARY 1, 1911.

System.	Plant location.	Name of company.	No. of installments.	Date put in operation.	No. of ovens.	Uses of coke.	Uses of surplus gas.
Semet-Solvay	Ensley, Ala.	Tennessee Coal, Iron and R. R. Co.	First Second	Oct. 1898 Mar. 1902	120 } 120 }	Blast furnace	Fuel gas
Semet-Solvay	Tuscaloosa, Ala.	Central Iron & Coal Co.	First	Feb. 1906	40	Blast furnace	Fuel gas
Semet-Solvay	S. Chicago, Ill.	By-products Coke Corporation	First Second Third	Dec. 1905 Dec. 1906 Dec. 1910	120 } 40 } 40 }	Blast furnace, foundry and domestic.	Illuminating
Semet-Solvay	Delray, Mich.	The Solvay Process Co.	First Second Third Fourth	Sept. 1901 Nov. 1902 Mar. 1906 Mar. 1909	30 } 30 } 60 } 12 }	Furnace, foundry, domestic and lime-burning.	Illuminating
Semet-Solvay	Syracuse, N. Y.	The Solvay Process Co.	First Second Third	Jan. 1893 Jan. 1896 Jan. 1900-1903	12 } 13 } 15 }	Lime-burning and foundry.	Fuel
Semet-Solvay	Geneva, N. Y.	Empire Coke Co.	First Second Third	Aug. 1904 Aug. 1909 Aug. 1910	30 } 16 } 49 }	Foundry and domestic.	Illuminating
Semet-Solvay	Cleveland, O.	Cleveland Furnace Co.	First	Aug. 1896	50 }	Blast furnace	Fuel gas
Semet-Solvay	Dunbar, Pa.	The Dunbar Furnace Co.	Second	July 1903	60 }	Blast furnace	Fuel gas
Semet-Solvay	Chester, Pa.	Philadelphia Suburban Gas and E. Co.	First	April 1904	40	Blast furnace.	Illuminating
Semet-Solvay	Lebanon, Pa.	Pennsylvania Steel Co.	First	July 1904	90	Furnace and gas.	Fuel and gas engines
Semet-Solvay	Steelton, Pa.	Pennsylvania Steel Co.	First	Jan. 1907	120	Blast furnace	Fuel gas
Semet-Solvay	Benwood, W. Va.	National Tube Co.	First Second	Oct. 1898 Mar. 1901	60 } 60 }	Blast furnace	Fuel gas
Semet-Solvay	Milwaukee, Wis.	Milwaukee Coke & Coal Co.	First Second	Mar. 1904 Mar. 1906	80 } 80 }	Blast furnace, foundry and domestic.	Illuminating
Koppers	Woodward, Ala.	Woodward Iron Co.	First	1910	60 ²	Blast furnace.	Fuel and power
Koppers	Corey, Ala.	Tennessee Coal, Iron & R. R. Co.	First	1910	280 ²	Blast furnace.	Fuel and power
Koppers	Joliet, Ill.	Illinois Steel Co.	First Second	1908 Mar. 1909	140 } 140 }	Blast furnace.	Fuel and power
Koppers	Gary, Ind.	Illinois Steel Co.	First	1909	560 ²	Blast furnace.	Fuel and power
United-Otto	Indianapolis, Ind.	Citizens Gas Co.	First	1909	50	Blast furnace and foundry.	Illuminating
United-Otto	Sparrows Pt., Md.	Maryland Steel Co.	First	Mar. 1903	200	Blast furnace.	Illuminating
United-Otto	Wyandotte, Mich.	Michigan Alkali Co.	First Second	Oct. 1902 Aug. 1906	15 } 15 }	Burning limestone.	Fuel gas
United-Otto	Duluth, Minn.	Zenith Furnace Co.	First	July 1904	50	Blast furnace.	Illuminating
United-Otto	Camden, N. J.	Camden Coke Co.	Second	July 1906	50	Foundry and domestic.	Illuminating
United-Otto	Buffalo, N. Y.	Lackawanna Steel Co.	First	May 1904	564 ¹	Blast furnace	Fuel gas
United-Otto	Hamilton, O.	Hamilton Otto Coke Co.	Second	May 1909	50	Blast furnace.	Illuminating and power
United-Otto	S. Sharon, Pa.	Carnegie Steel Co.	First	July 1903	212	Blast furnace.	Illuminating
United-Otto	Johnstown, Pa.	Cambria Steel Co.	Second Third Fourth	Mar. 1899 Sept. 1904 Feb. 1907	100 } 100 } 112 }	Blast furnace.	Fuel gas and power
Otto-Hoffman	Everett, Mass.	New England Gas & Coke Co.	First	June 1899	400	Domestic, industrial and locomotive.	Illuminating and power
Otto-Hoffman	Camden, N. J.	Camden Coke Co.	First	Jan. 1903	100	Blast furnace.	Illuminating and fuel
Otto-Hoffman	Hamilton, O.	Hamilton Otto Coke Co.	First	April 1901	50	Domestic and foundry.	Illuminating power
Otto-Hoffman	Glassport, Pa.	United Coke & Coal Co.	First	Feb. 1897	120	Blast furnace and domestic.	Illuminating and fuel
Otto-Hoffman	Johnstown, Pa.	Cambria Steel Co.	First	Nov. 1895	60	Blast furnace.	Fuel and power
Otto-Hoffman	Lebanon, Pa.	Lackawanna Iron & Steel Co.	First	Mar. 1903	232	Blast furnace.	Fuel gas
Rothberg	Cleveland, O.	Cleveland Furnace Co.	Second	Oct. 1907	25	Blast furnace.	Illuminating and power
Rothberg	Buffalo, N. Y.	Lackawanna Iron & Steel Co.	First	May 1903	282	Blast furnace.	Fuel gas
Rothberg	Lebanon, Pa.	Lackawanna Iron & Steel Co.	First	May 1903	5		
Didier	S. Bethlehem, Pa.	Lehigh Coke Co.	First	May 1903	300 ²		

¹ Contracted for; 188 Completed.² Not completed.

hive ovens, it may be shown that the 34,635,000 tons of coke made in beehive ovens from 52,400,000 tons of coal could have been made in by-product ovens with 47,430,000 tons; or 4,970,000 tons would have been saved, would not have been mined; our mines would have been conserved to this extent and the life of the mines so much lengthened.

Further, for a ton of coal coked in by-product ovens there is gas available as fuel in the steel plant amounting to 4,000-5,000 cubic ft. This amount of gas is the equivalent in the steel mill of 200 lbs. of coal, or, with coal at \$1.75, is worth 17.5 cents. There is, therefore, not only a saving in coal used for coking, but there would be a saving in the coal used as fuel. This would amount to 200 lbs. for every ton of coal coked in by-product ovens. We have shown above that 47,430,000 tons is the coal required in by-product ovens to take the place of the larger amount coked in 1910 in beehive ovens. Hence, the coal equivalent for the total gas saved would be 4,743,000 tons. This added to the amount of coal saved because of higher yield of coke, we have a total saving of 9,713,000 tons of coal which could have been left in the mine in 1910 and this reduced supply of coke and coal would have been adequate for the demand.

If the Federal Government is serious in its purpose to conserve our coal resources it may do so by ruling that additional coking capacity in the future shall be of the by-product type. The average increase per annum in the past 10 years of coke production has been 2,000,000 tons. This increase would be taken care of by the building of 600 modern by-product ovens. If by-product coke is to take the place of anthracite coal for domestic fuel, as in certain places it is rapidly doing, the increase per annum will be more than 2,000,000 tons.

There seems to be among iron manufacturers, who have installed large numbers of by-product ovens, a tendency to have them in sufficient number to supply their minimum demands for coke, while the difference between the minimum and maximum is perhaps more economically supplied by beehive ovens which are a much smaller unit and may be shut down and remain idle and again started up without excessive loss or deterioration. There are in the United States 100,000 beehive ovens, 47,000 of which have been built in the last 10 years. As the life of a beehive oven is supposed to be 10-12 years, it would appear that a very large number of beehive ovens would soon be useless. Another feature of the by-product coking industry which must not escape consideration, is the increasing tendency of the illuminating gas manufacturers to look with favor upon the byproduct coke oven as a valuable substitute for the small gas retort, particularly when the source of heat for coking this coal is cheap coal in a producer, for when thus operated 10,000 cubic ft. of gas is available instead of 4,500. Further, it may ultimately drive out the water gas plant, which now usually exists in illuminating gas

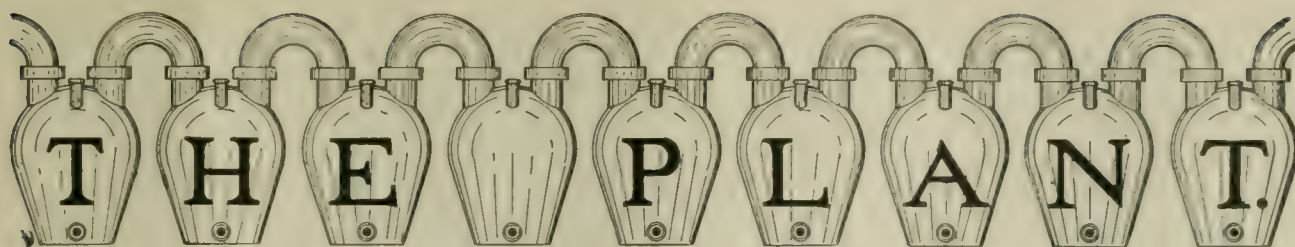
plants to furnish 50 per cent of the producing capacity, for its coke is of superior quality to the ordinary gas house coke and may be used for foundry purposes, and if it is sold for such purposes there will be none for the making of water gas.

It is difficult to predict the future of any industry and determine how much longer this devastating beehive coke manufacture will exist and the unnecessary loss of valuable nitrogen continue, but in the face of the crying needs of the soil, which have brought about a world's shortage of available nitrogen in spite of the placing of about 59,000 tons of cyanamide on the market, several thousand tons of Norwegian saltpeter (CaNO_3), a small production from the Haber process ($\text{N} + \text{H}$), and the very large increase in the world's production of ammonium sulphate, there will certainly be a rapid substitution of the by-product for the beehive oven. It is not unreasonable to expect that the government returns at the completion of this decade will show that 50 per cent of the coke used in this country will come from by-product ovens; certainly the great increase in importation of ammonium sulphate in 1911, from 63,000-105,000 tons, 66 per cent, while the domestic production went from 116,000-130,000, or an increase of 12 per cent, coupled with the increase of price from 2.8 cents per lb. to 3.05 cts. would warrant an expansion in the by-product coke industry.

A statement of the condition of the by-product coke industry upon Jan. 1, 1911, according to Mr. E. W. Parker, is found on the preceding page.

The mine production of gold, silver, copper, and zinc in Tennessee in 1911, according to H. D. McCaskey, of the U. S. Geological Survey, was valued at \$2,551,774, an increase of \$262,043 over the value for these metals in 1910. The gold production was 562.17 fine ounces, valued at \$11,621; the silver 106,660 fine ounces, valued at \$56,530; the copper 18,850.276 lbs., valued at \$2,356,285; and the zinc, figured as spelter, 2,234,000 lbs., valued at \$127,338. When compared with the corresponding figures for 1910 the above figures show an increase of \$8,508 in gold and of 25,421 fine ounces of silver, 2,012,549 lbs. of copper, and 301,445 lbs. of zinc. A total of 604,538 short tons of ore was mined in 1911, of which 581,974 tons were copper ore and 22,564 tons were zinc ore. In 1910 the quantities mined were 552,796 tons of copper ore and 25,638 tons of zinc ore.

Mr. John Germain Porter has resigned his professorship in the University of Cincinnati and will devote his time to consulting practice as metallurgical and chemical engineer, with special reference to the operating efficiency of blast furnace foundry coking and other processes. His headquarters will be at Staunton, Va., and in such work he will co-operate with Mr. Charles Catlett, geologist and chemist, of that city.



WATER FILTRATION FOR INDUSTRIAL PURPOSES.*

By CHURCHILL HUNGERFORD, FILTRATION ENGINEER.

It is frequently a matter of surprise to otherwise well informed persons that the ordinary standards of purity required in drinking water are sometimes not nearly as severe as those required in water used for industrial purposes. Nevertheless, this is true in many instances because the water contains certain substances which are perfectly harmless to the human system but possess chemical affinities for other substances used in the arts and industries that create very annoying disturbances, indeed. On the other hand, many waters that have been so highly contaminated by sewage and industrial wastes that no form of purification would make them suitable for drinking purposes, can be made eminently satisfactory for industrial purposes. It is a by no means uncommon condition to find a manufactory unable to use the city supply, which may be justly considered especially fine from a potable standpoint, yet by means of an efficient purification plant be able to get perfect satisfaction from a polluted stream which receives the sewage and industrial waste of the town itself.

Disregarding the hardness of the water, the reduction of which is not properly a function of filtration, there are a number of apparently harmless forms of pollution that are very troublesome in many instances.

The writer has in mind a rather remarkable case in a New York village of a manufactory wherein very gorgeously printed lap robes are made. This concern has been in business a great many years, and the designs, which are quite ornate and many colored, are hand printed by large wooden blocks with certain colors imported from England, supposed to be secret mixtures. These colors are all mordanted with alum. In fact, the robes themselves are passed through quite a strong solution of alum at one period of their manufacture, and are then dried. They are finally washed, and at this point the trouble manifests itself in a rather singular manner. As soon as the water commences to get warm, or during the latter part of May, the light colors commence to get flat and as the season progresses and hot weather comes on, much of the detail is altogether lost and the whites and light shades commence to assume a yellowish cast. The wise men of the block printers shake their heads and say their secret colors are affected by the warm water, and as

a result robes of a dark shade only can be made during the warm weather.

An investigation of the water supply elicited the information that the major part of it is derived from a shallow lake, about seven miles back in the country. The elevation of the water in this lake had been raised 4 or 5 ft. a number of years ago and overflows a peat-bog over a square mile in extent. During the winter it is customary to close the outlet of this lake and allow it to fill up. About the latter part of May, when the water in the stream begins to get low, the gates are opened and the highly colored water from the lake takes the place of the comparatively clear flow. When this colored water reaches the mill and the alum saturated lap robes are washed in it, the coloring matter derived from the peat is precipitated by the alum on the fibre, and the more color there is to the water the greater the discoloration of the goods. Moreover, the drainage area of the lake being comparatively small and the drain upon the lake heavy, the water keeps getting lower and lower until part of the peat-bog is exposed and the water percolating from this causes the lake supply to grow continually darker until the fall rains refill the lake. It can be seen by this that the color of the water and not the temperature is entirely responsible for the apparently bad behavior of the dyes. The above is a harmless but not too attractive city supply.

Another instance is in a city of some 60,000 inhabitants supplied from a fairly large stream. The water from this stream possesses considerable color and is filtered by means of a mechanical filter plant. This mechanical filter plant is very well operated, indeed, shows a very high bacterial efficiency and is ideal in every particular save one, and that is that for some reason or other a small amount of hydrate of alumina, formed during the chemical treatment of the water with alum, finds its way through the filters. This has no hygienic significance whatever and the inhabitants of the town are enthusiastic over the many virtues of their filter plant, insofar as the potability and appearance of the water is concerned. However, there are a number of large silk dye works in this town and this trace of hydrate of alumina present in the water prohibits its use in silk dyeing. Most of the dye houses are located along the banks of the same stream from which the city supply is drawn, but at a point below town. The stream at this point is not only badly contaminated with sewage, but the discharge from the silk dye houses themselves enters into it, making the general color of the water blue-

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black. Nevertheless, the silk dyers have solved the problem of water supply by filtering this badly contaminated water with a filter which will not permit hydrate of alumina to pass through it. The filtered water is, of course, crystal, clear and entirely free from dye.

Still, again, the anaemic person who spends some weeks at a high-priced sanitarium, drinking chalybeate waters with the hope of bringing the iron content of his system up to the normal 26 or 27 grammes which it should contain, would probably be quite indignant if told that the water he is drinking in such quantities is not even fit for laundry purposes.

Originally, filtration for industrial purposes meant the removal of clay, silt and vegetable stains from the water. The problem at that time was a simple one, as it merely meant that enough alum or sulphate of alumina or similar coagulant was employed as a preliminary treatment, after which the water could be passed through the filters and would be suitable for industrial purposes.

However, as the country became more populated, its manufactories larger and more numerous, the streams commenced to show considerable quantities of various forms of industrial wastes and sewage. The industrial wastes consisted very largely of dye stuffs, waste liquors from paper and pulp mills, chemical wastes from wire-drawing plants, gas-house liquors, tannery wastes, etc. Some streams contained only one or two different varieties of contamination, while others contained several. This condition has increased with the population until most of the streams in the east are greatly discolored and are badly polluted with sewage. Moreover, most of the available sources of pure water have been preempted by municipalities for their water supplies.

Cheap water is imperative in the present day to the manufacturer. He cannot afford to pay from 4 to 35 cts. per 1,000 gals. to the municipality for several million gallons of water per day, and he is perforce driven to the polluted streams, his only alternative being to place his establishment at so remote a point that it becomes difficult of access and almost impossible to procure labor. Naturally he chooses the situation of his plant with reference to the availability of labor and the propinquity of the market. The vital question that then comes before him is, can the highly polluted water supply which is available be made suitable for his purposes? The answer to this question in ninety-nine cases out of one hundred is in the affirmative. It can be done and done well. Moreover, in large plants the average cost of treatment can be kept well below \$3.50 per million gallons, or, say, one-third of one cent per thousand gallons, as against the 4 to 35 cts. per 1,000 gals. the manufacturer would be compelled to pay to the municipality.

Such conditions as the last represent perhaps 75 per cent of the problems of industrial filtration at the

present day, and the percentage is continually increasing.

The problems involved in such waters, especially when contaminated by many different substances, become complex in their nature. True, the old standby, sulphate of alumina, still figures very extensively in all such plants, but there are many conditions wherein the use of sulphate of alumina alone as a preliminary treatment leads to a downright failure of the filter plant to accomplish the desired aims. To reach perfect results an intimate knowledge of the contamination must be reached. Chemical analysis, of course, tells us much and a bacteriological analysis is also necessary in some cases, but an actual survey of the conditions to be met must be made before an intelligent purification plant can be constructed.

In making this survey it is necessary, particularly on a comparatively small stream, to notice the particular hours at which certain industries discharge the most waste; to note the particular character of the most important of these wastes and to further note very particularly the influence that one set of industrial wastes will have upon another. For instance, the waste dye from a woolen mill, mingling with the waste soap from the fulling and finishing department, eventually come into contact with the lime existing in the water, with the result that not only the soap is precipitated but a very considerable portion of the coloring matter is also carried down. Further down stream we may strike the waste from a wire drawing works, or similar industry, wherein sulphate of iron enters the water. This combines very actively with the coloring matter and forms a heavy precipitation. At the same time large quantities of domestic sewage are being discharged into the stream. This commences to ferment very rapidly. Portions of it are liquified and other portions precipitated. Bacteria become very active in the stream unless some poisonous or antiseptic substance is being discharged in it. By the time the water has reached the consumer possibly as high as seventy-five per cent of the dissolved matter that had been discharged into the stream in a precipitated form, thereby lessening the load on the purification plant by that amount.

Now, after having considered all these points, we come to the operation of the plant itself. In the first place, we wish to get rid of the already precipitated matter as economically and as efficiently as possible. In the next place, we must precipitate as cheaply as possible the remaining deleterious substances. As above stated, the most economical and effective substance for doing the major part of this work is sulphate of alumina. The writer realizes that here will be considerable protest made in favor of sulphate of iron and lime. Nevertheless, so far as his own experience goes, and, in fact, the experience of some others, sulphate of alumina is cheaper, safer, more satisfactory and far easier to apply than sulphate of iron and lime.

Having applied the sulphate of alumina with a due

regard for the alkalinity of the water as evinced by the chemical analysis, the treated water is allowed to flow slowly through a settling tank. The period of time occupied in sedimentation varies greatly with different waters. In some cases one and one-half hours may be sufficient. In others, three hours. Occasionally twelve hours are required, and we know of one instance in which six days' sedimentation is employed. In the latter instance chemicals are not used, the biological conversion of the organic matter being aimed at. Generally speaking, however, three hours' sedimentation with aluminum sulphate for a coagulant is sufficient.

We occasionally find, however, upon operating a plant that complete decoloration of the water is not effected and that there is a very offensive odor. Moreover, strange things are taking place in the settling basin. As we look at it, we see large masses of sediment rise from the depths, come to the surface, spread out and disappear. One point in the sedimentation basin will show a fairly good degree of sedimentation, while further along where sedimentation ought to be further advanced we find the water far more turbid than when first introduced into the basin. The sewage in the water is simply fermenting and this fermentation is not only interfering with sedimentation by reason of the gases evolved, but is producing resolution of the impurities entrapped by the hydrate of alumina. In other words, we are undoing the good work we have done. Moreover, the volume of the impurities going to the filter is far greater than it should be, and the filters are requiring altogether too frequent washing.

Shortly after a very singular manifestation takes place. The filters, which have been delivering a gradually deteriorating effluent, finally refuse to deliver any water at all. An examination of the sand after washing shows it to be perfectly clean, and there is no apparent reason why the water should not pass through. Nevertheless, the filters are nearly impervious. A more thorough examination develops the fact that the pipes in the underdrains of the filters have become completely filled with a fungus growth, usually *beggiatoa* or sewage fungus. We clean it out and in a few days the same conditions occur again; the water that does come through it is unusable.

The above conditions might take place in a filter plant provided we were confined to sulphate of alumina. However, with a knowledge of troubles about to occur, we can guard against them by taking the proper precautions. The Imhoff tank, which has been recently so successful in the removal of sludge from sewage, might be applicable in this case, but there is a considerable doubt in the writer's mind whether complete decolorization of the water could be effected by filtration after the water had passed through such an apparatus without a subsequent chemical treatment. It is necessary to stop the fermentation of the precipitated matter. We can often do this by the addition

of copper sulphate in fairly large proportions, say, for instance, two or three parts to the million. This in certain cases is sufficient. The fermentation stops, sedimentation is good, the growths in the pipes gradually disappear, the effluent of the filter becomes clear, sparkling and odorless and everything is satisfactory. However, there are many cases where copper sulphate cannot be used in sufficient quantities, or where it is not useful at all. Where the percentage of sewage is very high we find that there is much undecomposed and unprecipitated organic matter in the water, and to get really satisfactory results it must be consumed in some manner. Some powerful oxidizing agent is required. In such instances calcium hypochlorite recommends itself. This is to be used very judiciously, as a very faint excess, indeed, would produce the most disastrous results in dyeing, and when accurately applied it consumes the dissolved organic matter as thoroughly and as effectually as if it were dried and burned in a fire. Moreover, it is a tremendously powerful bactericide and a bacterial analysis of the treated water shows it to be almost sterile even before filtration.

At Passaic, N. J., using Passaic River water, which runs about one million bacteria per cubic centimetre, or equal to ordinary sewage, it was found that with two parts per million of calcium hypochlorite and five hours' sedimentation the bacteria ranged from twenty-seven to one hundred per cubic centimetre, and that so long as the hypochlorite was used there was no tendency whatever of the sludge at the bottom of the basin to ferment.

In most plants the amount of hypochlorite employed ranges from one to three parts per million. Where fermentation is interfering with sedimentation it must be applied as the water enters the sedimentation basin, but if sedimentation is reasonably good an economy can be effected by applying the calcium hypochlorite after sedimentation is completed. By following this procedure much of the oxidizable matter that would be precipitated by the alum has settled to the bottom and the principal oxidizing activity of the hypochlorite is directed against the dissolved matter and the bacteria.

Another action of the calcium hypochlorite is to decolorize the dyes that may have resisted action of the aluminum sulphate. This action, however, is not especially important, as the strength required to produce this result is usually greater than is safe to use.

Needless to say, the treated water must show no trace whatever of free calcium hypochlorite, and the only logical way of attaining this result is to keep the quantity of chemical applied at such a point that its energy will be entirely expended upon the organic matter. An accurate chemical feed is of the utmost importance when using the calcium hypochlorite.

With certain waters it is found that although a suitable degree of precipitation is obtained by the use of the aluminum sulphate the precipitate is of a flocculent, buoyant nature and will not settle. In fact, it has

a tendency to come to the surface of the water. On examination it will be found that the buoyant tendency of the precipitate is due to small bubbles of carbonic acid gas given off in the reaction between the sulphate of alumina and the earthy carbonates. If the water is soft this tendency is corrected by adding either shortly before the application of the aluminum sulphate, or shortly after, a small quantity of calcium hydrate. This calcium hydrate absorbs the free carbonic acid gas with great avidity and the flocculent precipitate falls to the bottom of the settling basin at as rapid a rate as could be desired.

In the above example we have mentioned the beneficial action that takes place in the tendency of one set of wastes to neutralize another; the treatment with sulphate of alumina to produce precipitation and sedimentation; the additional treatment by antiseptics to prevent further bacterial action and to prohibit the growth of other objectionable vegetable organisms and the oxidization of the excess of organic matter.

There is still another feature to be considered, which is of especial importance on small streams to which at times extremely large quantities of defiling matters may be discharged for short periods of time, and that is the advisability of directly avoiding this extreme contamination, or producing such a degree of delution that the problem involved is a very slight one.

The writer has in mind a small stream on which is located a paper mill. A few hundred feet below this paper mill is a felt mill, drawing its supply from the same stream, the flow of which runs as low in dry weather as one and one-half million gallons per day. At certain irregular periods the digesters containing large quantities of free caustic soda, together with the saponified grease, resin, pectin and various other substances extracted from the rags, etc., are discharged into the stream. This proportion of impurities at the time of discharge is so great that the alkalinity of the hundred parts and the basin below the dam where the water falls over is frequently filled to a depth of 6 ft. with what appears to be soap suds.

The effect of alkali upon wool is disastrous and the felt mill experienced great trouble with the soda. They even went to the trouble of stationing a man at their head gate, some eight or nine hundred feet above their mill, with instructions to close it at such times as he saw the digester discharge coming down. As soon as this substance had passed by, usually a period of not more than twenty minutes, the gate was opened again, the head race holding enough water to supply the mill in the interim. This was manifestly a clumsy way of avoiding the trouble. The real solution of the problem was worked out in the following manner: At the lower end of the head race near the mill a settling reservoir holding a half million gallons of water was constructed at such an elevation that the water flowed by gravity into it. The water for the mill was drawn from the opposite side of the reservoir to the point at which it entered. The amount of strongly alkaline water enter-

ing this reservoir was so small in proportion to the entire body of water in it that it not only had no deleterious effect but the alkali actually tended to soften the main body of water in the reservoir.

The point I wish to make in this connection is, that only a small amount of the highly alkaline water enters the reservoir, the major portion of it passing the inlet and going down stream, the quantity entering the reservoir being such a small portion of the whole body of water that even if it had no beneficial effect it would be so greatly diluted that its treatment would be a very small matter.

The quantity of water required in the various industries is very great in comparison to the requirements of municipalities. For instance, a supply of two million gallons per day would furnish a town of 20,000 inhabitants, a small paper mill of, say, twenty tons daily output, a very small bleachery, or a small silk dye works. The largest dye works in this country consumes 23,000,000 gallons of water a day and a contract has just been let for a bleachery in the New England States requiring a filter plant having a capacity of 36,000,000 gallons per day. This is approximately the amount of water used by the city of Philadelphia west of the Schuylkill. These figures seem stupendous to the person who has not studied industrial requirements.

A pound of muslin, or similar cotton fabric, requires in the bleaching process about 27 gals. of water. A pound of paper requires about 54 gals. of water, and a pound of silk not less than 1,000 gals. of water. Moreover, many of these processes in which water occupies such an important part include very delicate chemical reactions in which strong acids and alkalies play their part.

The dyeing of silk in the skein is an interesting example of the importance of a sufficiency of very good water. The dyer received a quantity of silk and some sample colors. Say, for instance, one hundred pounds of silk are delivered to him to be dyed a pale blue and white. He receives instructions to return two hundred pounds of silk. The first operation through which the skein is put is to place it in a bath of soapy water and boil it for a period of time. This removes the natural gum or seracine from the fibre, and after drying it is found that the one hundred pounds of silk now weighs but seventy-five.

The next process is to make this seventy-five pounds of silk weigh two hundred pounds. This is effected by hanging the silk in a bath of bichloride of tin. After a certain period of time the dyer estimates the fibre of the silk has absorbed enough tin to weigh the necessary two hundred pounds. This is not a deposit of a metallic salt upon the fibre, but is a chemical combination that has taken place between the fibre and the tin. It cannot be washed off nor out, and practically the only process by which the tin could be separated would be by burning the silk. This bichloride of tin is a very corrosive substance and the silk cannot be

handled with the naked hand until after it has been washed to remove the excess. Washing is effected by hanging the skeins over the revolving rolls of a washing machine, against which thousands of needle-like jets of water are directed. After this washing the silk is treated with a dilute solution of sodium phosphate and is again run through the washing machine. If the silk has not taken up enough tin to reach the desired weight it is again placed in the tin bath and the same process is gone through, sometimes a half dozen treatments being required to gain the requisite weight.

The dyeing of the silk, either white or colored, is usually done in a hot soap bath, to which the dye is added, and to give additional body to the bath a part of the seracine extracted from the silk in the early part of the process is put in it. It is not customary in this country to bleach silk, the white being produced by dyeing it purple and exhausting the color in an acid bath. This is done by dyeing the silk red and blue and the shade of white eventually evolved depends upon the proportions of red and blue used. This dyeing process is rather mysterious to the uninitiated. The dyes used are not faint red and blues, but when mingled produce an intense purple which, of course, is deposited on the silk. The immersing of these purple skeins in the acid bath and the rapid transition from purple to silvery white is a most interesting and attractive process.

After a period of time in the acid bath, during which the scroop, the trade name for that property which gives to silk its rustle, is formed, the skeins are again washed and passed through the hydro-extractor, after which they are placed in a steam-tight compartment, stretched under a pull of several thousand pounds and live steam turned in on them for a minute or so. They are then taken out, hung over a smooth stick, twisted, yanked and otherwise mauled by a strong determined man for two or three minutes. This terminates the dyeing process and the dull yellow, linen-like skein, not half as big around as one's wrist, has been converted into a silvery fluffy mass of shining fibre at least four times its original bulk, for during the absorption of the weighting materials the silk has increased greatly in volume.

The owner of the silk then receives the two hundred pounds of silk for the one hundred delivered, which seems very much like getting something for nothing until you realize that the dyer gets anywhere from \$1.50 to \$3.50 per pound on what he returns for his pay.

It is possible to weigh a pound of raw silk up to sixty ounces, so that little more than twenty per cent of the fibre itself is silk, the rest being weighting substance. Needless to say, the wearing value of such silk is almost nothing.

In the above process large quantities of water are used in the boiling off of the seracine. Soft water is desirable, as it prevents the formation of lime soaps.

In the washing, after the bichloride of tin bath, the water must be absolutely bright and colorless and is preferably hard from earthy carbonates. Any trace of color in this water will be immediately precipitated by the acid upon the silk and produce a stain. Then, again, after being placed in the sodium phosphate bath if there were any trace of color or vegetable matter in the water it would be precipitated upon the silk fibre in such a manner as to act as a resist in the subsequent dyeing process with the result that streaky skeins would be produced. This tendency is so strong that even jet black silk will show streaks in it if the water is not perfect.

Perhaps the most important point of all is the acid bath, in which most skein silk of every color is placed to produce the scroop. If there is any trace of color in this water, to which a small amount of acetic acid has been added, when the skeins are placed in it, this color will deposit itself upon the silk in the most incredible manner, and a skein dipped a few times in this water will come out very much off color. This tendency of the color to deposit itself on the fibre is so strong that when the water does not appear right to the dyer, without any further instructions he takes a batch of silk which is to be dyed a dark color and runs it first through this acid bath so that all of the color will be precipitated upon it, after which he can place his light colors and whites in it with impunity.

Still another dangerous point is the final washing of the silk after removing it from the acid bath. This wash water must naturally be very pure as otherwise we would have a deposit upon the silk from it.

Until a comparatively recent time nothing but spring or well water was used for the whites and light colors. There is one silk dye works in Paterson, N. J., that has seventy-five 8-inch artesian wells, none of which are less than three hundred and fifty feet in depth, all of them drilled through the red sandstone.

So much has been said in this article about forms of contamination by industrial wastes and the benefits of filtered water that possibly a brief description of the two general types of filter plants would be interesting.

There are two kinds of filters, pressure and gravity. Really they are identical in operation, the only difference being in their application. The pressure filter is the same device as the gravity filter excepting that it is placed in an enclosed steel tank and operates under whatever pressure the service main may carry, delivering its water filtered and still under pressure with a loss of head ranging from two to ten pounds, depending upon the make of filter.

The gravity filter on the other hand relies upon the weight of water on it to drive the water through the bed and the water is discharged at the bottom under no pressure.

Taking the detailed parts of a gravity filter plant for an example, we find that they consist of a chemical feed, a settling basin with the necessary baffles,

the filter proper and the machinery for washing the filter. As the consumption of every industry varies more or less from moment to moment there are fluctuations in the rate of flow of the raw water coming to the settling basin. The chemical feed must be an apparatus that will regulate whatever chemicals are being applied to meet this fluctuation. For instance, if the feed is set to apply two grains of sulphate of alumina and one-eighth of a grain of calcium hypochlorite per gallon of water it must do that and exactly that, whether the plant is running at full speed, one-quarter speed or a twenty-five per cent overload. It is a small but vital part of the entire plant and might be compared in its way to the governor of a steam engine. Of course, chemicals are applied in the form of solutions of a definite strength.

The water after receiving its dose of chemicals flows through the settling tank in a continuous process, in at one end and out at the other. To stop the tendency of the water to flow directly across the basin from inlet to outlet leaving a large eddy on either side, baffles are placed so as to compel the entire body of water to take a circuitous course through the basin. Much of the solid substance in the water has already been coagulated by the action of one set of impurities upon another, and the applied chemicals have produced further precipitation and have, moreover, gathered together the finer particles of suspended matter into comparatively large masses so that all settle with considerable rapidity toward the bottom of the basin, where they remain until such time as it is convenient to remove them. The hypochlorite used is sufficient to prevent fermentation if the water is highly contaminated with sewage. Moreover, the alum applied has exhausted such remaining dyes as have not been precipitated prior to the time it was added.

Finally the water reaches the far end of the settling basin. It is much clearer, has much less color, the odor has practically disappeared and there seems to be a decided improvement in every way. It is far from being fit for use, however. It is then conducted to the filters through the necessary pipes, passes down through them and every trace of suspended matter is removed with the result that water that three hours before was very dark in color, had a strong odor of sewage and contained much suspended matter, is as bright, sparkling and clear as the clearest spring water, and, so far as the senses can determine, is its equal in every way.

The three essential parts of a filter itself are the case, the filter bed proper and the strainer system. The case is of either steel, wood or concrete. The filter bed itself is of carefully selected sand and the strainer system, which consists of a series of pipes leading to all parts of the bed terminating at their outer ends in strainers or sand valves, devices which have slots or perforations of too small a size to permit the sand to pass through, but sufficient in number

to allow a definite quantity of water to leave the sand bed.

This strainer system is placed on the floor of the filter, and its object is not only to collect the filtered water from the bottom of the filter but also to distribute the wash water uniformly underneath the bed during the washing process.

Considerable quantities of sulphate of alumina and some hypochlorite of lime have been used. As any trace of either of these substances in the filtered water would utterly condemn it for almost every industrial purpose they must be removed or converted into innocuous substances. This is effected in the following manner: Referring first to the sulphate of alumina, a previous analysis of the water has been made which shows the amount of its alkalinity. For every ten parts per million of alkalinity that the water contains one grain of sulphate of alumina per gallon can be used with safety, because this quantity of the alkali will combine with the alum to convert it into an insoluble substance, hydrate of alumina, which is readily removed by the filters, and the sulphate of lime. In other words, the carbonate of lime existing in the water renders the alum insoluble and converts it into a form in which the filter can hold it. Occasionally we find a water, particularly in the New England states, so soft that it does not possess sufficient alkalinity to permit the use of alum in sufficient quantities to produce the desired result. In such an event an artificial alkalinity is produced by the addition of a small amount of carbonate of soda or by the introduction of corresponding quantities of quicklime.

Calcium hypochlorite, chloride of lime or bleaching powder, as it is variously known, on being mingled with the organic matter is decomposed into calcium chloride, and ozone is liberated in sufficient quantities to produce the necessary oxidization. Calcium chloride, being an inert salt and existing in such minute quantities has no significance from any industrial standpoint whatever. We thus see elimination of the applied chemicals or their metamorphosis into harmless and insignificant substances.

In addition to economy in the use of chemicals the other costs of operation such as attendance, power, etc., must be reduced to a minimum. One hour per day for each million gallons of water treated is sufficient to cover the attendance of a well designed industrial plant. The sedimentation basins are so arranged that the sludge drains into a channel passing down the middle connecting with a blow-off valve. Opening this valve at intervals of one to six months and permitting the entire chamber to drain takes care of most of the sludge.

The filters must be so designed that they can be washed very rapidly and very thoroughly. This is done by simply reversing the current in the case of the filter pressure and forcing the water up through it at a high rate of speed. This causes the sand grains to dance up and down rapidly, each scouring the other

so that after a few minutes the entire sand bed is cleansed.

In gravity plants an economy in washing can be effected by inducing an additional agitation of the sand either by means of a revolving rake or by forcing compressed air under the entire filter bed. Either of these processes produce the same result, that is, very rapid motion of the sand grains and a consequent rapid loosening of the retained impurities.

All types of filters are connected directly with the drain so that wash water can flow to it. Moreover, the first water that comes from the filter after washing is of poor quality and it is customary to filter into the drain for a minute or two or until the filter bed gets thoroughly packed. Depending upon its design, an ordinary filter will wash in from five minutes to an hour's time, and will consume from two to fifty per cent of the water filtered for washing. The general type of filter used for industrial purposes, however, is designed to be washed very quickly.

From the above it will be seen that the chemical treatment in many industrial problems is as essential as the apparatus itself. Given a properly designed plant employing the proper chemicals, there is no reason why the most polluted American rivers cannot be made satisfactory for all industrial purposes.

The following matter is taken from the Berlin Export, the translation being by the Bureau of Trade Relations, Department of State: The English coal strike has brought up the question of how and to what extent coal can be replaced by liquid combustibles or other sources of power. The most favored countries in this respect are probably the Scandinavian, possessing, as they do, in their waterfalls a great source of power. Lately it has been found that the method worked out by a Swedish inventor of firing locomotives with pulverized peat is practical and economically just as advantageous as coal. However, the use of these resources, water power and peat, is confined to certain countries. It is different with petroleum, which is one of the generally available products of the world. The total production in America in 1911 was approximately 83,000,000 barrels. In Russia the slackening of the output of the wells in the Baku region became decidedly apparent last year, showing a decrease from 478,000,000 to 427,000,000 poods (57,382,953 to 51,260,504 barrels). The total production of Russian petroleum declined as compared with 1910 by 28,000,000 poods (3,361,345 barrels), and amounted to 554,000,000 poods (66,506,603 barrels). Roumania produced in 1911 somewhat more than 1,500,000 tons (10,785,000 barrels), and exported about 700,000 tons (5,033,000 barrels). As is well known, the industry is carried on almost exclusively with foreign capital, only 10,000,000 of the 28,000,000 marks (\$66,640,000) employed being Roumanian. Germany controls 58 per cent of the total capital. If

coal shall be replaced by petroleum to a considerable extent, it is clear that energetic measures will be necessary to provide suitable ships for the colossal transportation which may be expected. In England there are being built at present not less than 45 tank steamers with 800,000 tons loading capacity, but the demand for petroleum is increasing to such an extent that it hardly can be satisfied. England, for instance, imported last year 343,000,000 gallons (8,166,667 barrels), or 22,000,000 gallons (523,810 barrels) more than in 1910. The way in which these increasing amounts of petroleum are being used may be gathered from the fact that the imports of illuminating oil have decreased 20 per cent, whereas the imports of petroleum for power purposes have increased 150 per cent. The largest imports come from America, Russia being second, and Roumania third.

The "secondary metals" are those recovered from scrap metal, sweepings, skimmings, drosses, etc., and are so called to distinguish them from the metals derived from ore, which are termed "primary metals." The United States Geological Survey's figures, prepared by J. P. Dunlop, showing the recovery of secondary copper, lead, zinc, tin and antimony, are summarized in the tables below. The inquiry by the survey does not include the very large quantity of old iron and steel remelted, neither does it include the precious metals. The quantity of aluminum castings returned to secondary smelters is also increasing rapidly, a condition for which the automobile trade is largely responsible. That the value of the secondary metals, exclusive of gold, silver, platinum, iron, and aluminum, should reach the large total value of \$52,585,390 in one year is a fact not generally realized except by those interested in the purchase of metals.

The total value of the mine output of gold, silver, copper, lead, and zinc in the eastern or Appalachian states for the year 1911, according to H. D. McCaskey, of the U. S. Geological Survey, was \$11,787,942, against \$10,127,304 in 1910. This represents the production of 96 mines, of which 57 were gold placer mines—many of them very small. The total gold output from all mines was 7,709.52 fine ounces, valued at \$159,370, a decrease from 1910 of \$26,152, and the silver production (recovered entirely in refining the gold and copper produced) was 108,105 fine ounces, valued at \$57,296, an increase over 1910 of \$7,835. Of the gold output in 1911 the placer yielded 1,447.28 fine ounces, or nearly 19 per cent, the quartz ores 5,699.64 fine ounces, or 74 per cent, and the copper ores 562.60 fine ounces, or 7 per cent. This 7 per cent was derived from 801,842 short tons of copper ore mined, having an average gold and silver value of \$0.085 a ton against 774,040 tons in 1910, having a gold and silver value of \$0.076 a ton.

METALLURGY

CORROSION OF IRON AND STEEL.

Three papers dealing with corrosion were read before the meeting in London, England, on May 9, of the Iron and Steel Institute. Two of these were under the authorship of J. Newton Friend, J. Lloyd Bentley and Walter West, and the other was contributed by C. Chappell, Sheffield, and covered the "Influence of Carbon on the Corrodibility of Iron." One of the Friend-Bentley-West papers was entitled "The Mechanism of Corrosion," and discussed "The Corrosion Zone."

• Leading points of the three papers are given in The Iron Age as follows:

CORROSION OF NICKEL AND CHROMIUM STEELS.

The influence of nickel, and likewise that of chromium and of a mixture of nickel and chromium, upon the corrodity of steel was investigated. The steels were supplied in the form of bars and were tool-turned

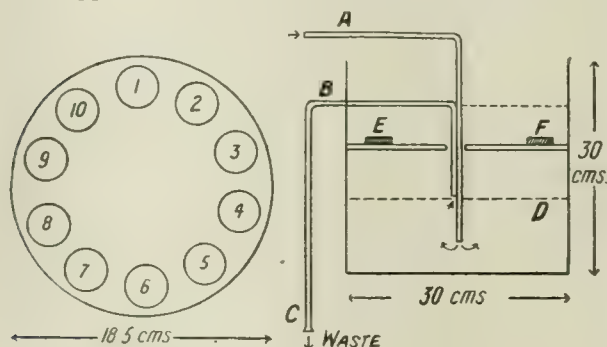


Fig. 1.

Fig. 2.

and sliced into disks 0.7 centimetre thick and 2.8 centimetres in diameter.

TABLE I.—ANALYSES OF STEEL DISKS INVESTIGATED.

Steel No.	Carbon per cent.	Silicon per cent.	Phosphorus per cent.	Manganese per cent.	Sulphur per cent.	Nickel per cent.	Chromium per cent.
1	0.29	0.14	0.023	0.39	0.024	..	..
2	0.39	0.208	0.023	0.685	0.036	..	..
3	0.19	..	..	0.29	..	3.72	..
4	0.24	..	..	0.46	..	6.14	..
5	0.08	..	..	0.38	..	26.24	..
6	0.32	..	..	0.36	..	..	1.12
7	0.11	..	..	0.110	..	..	3.58
8	0.09	..	..	trace	..	..	5.30
9	0.552	0.127	..	0.41	..	3.40	1.00
10	0.54	..	..	0.58	..	3.5	1.12

The disks were carefully polished with emery-paper, weighed, and subjected to corroding influences. They were laid flatwise on a circular sheet of paraffin wax in a glass crystallizing dish, as shown in Fig. 1, covered with faucet water to a depth of 6c. and kept in a dark cupboard to prevent any irregularity of corrosion consequent upon unequal illumination. The paraffin served to reduce to a minimum the possibility of

galvanic action, and also prevented the corrosive action of the silica—always observed if iron lies for any length of time in direct contact with glass. After 64 days the disks were removed, cleaned, and weighed, the loss in weight being taken as a measure of the corrosion. The results are given in Table II.

TABLE II.—CORROSION OF STEEL IN FAUCET WATER.

Steel No.	Nickel per cent.	Chromium per cent.	Original Weight, grammes.	Loss in Weight, grammes.	Corrosion factor.
1	..	..	35.6201	0.0961	100
2	..	..	37.4186	0.1038	108
3	3.72	..	33.5506	0.0798	83
4	6.14	..	30.1416	0.0666	69
5	26.24	..	33.4796	0.0488	51
6	..	1.12	28.7101	0.0817	85
7	..	3.58	28.6826	0.0558	58
8	..	5.30	31.1996	0.0400	43
9	3.4	1.00	30.8926	0.0736	77
10	3.5	1.12	31.5880	0.0844	87

Sea-water tests were then conducted in a precisely similar manner. After 64 days the loss in weight of the steels was found as given in Table III.

TABLE III.—CORROSION OF STEELS IN SEA WATER.

Steel No.	Nickel per cent.	Chromium per cent.	Original Weight, grammes.	Loss in Weight, grammes.	Corrosion factor.
1	..	..	34.4619	0.1136	100
2	..	..	37.5729	0.1196	105
3	3.72	..	30.9664	0.0886	77
4	6.14	..	32.9744	0.0906	79
5	26.24	..	30.2324	0.0516	45
6	..	1.12	28.7259	0.0686	60
7	..	3.58	25.9639	0.0291	26
8	..	5.30	30.9149	0.0261	23
9	3.4	1.00	30.6344	0.0936	82
10	3.5	1.12	29.1314	0.1026	90

Sulphuric acid tests were obtained in an exactly similar manner, the corroding liquid being 0.05 per cent sulphuric acid (that is, 0.5 g. of acid in 1,000 g. of solution with water). The results obtained after 60 days' exposure are given in Table IV.

TABLE IV.—CORROSION OF STEELS IN 0.05 PER CENT SULPHURIC ACID.

Steel No.	Nickel per cent.	Chromium per cent.	Original Weight, grammes.	Loss in Weight, grammes.	Corrosion factor.
1	..	..	37.9886	0.1594	100
2	..	..	37.2552	0.1560	98
3	3.72	..	32.2582	0.1350	85
4	6.14	..	31.8352	0.1320	82
5	26.24	..	31.4352	0.0860	54
6	..	1.12	29.2676	0.1134	71
7	..	3.58	29.9346	0.1088	68
8	..	5.30	30.8742	0.1086	68
9	3.4	1.00	30.8136	0.1394	87
10	3.5	1.12	32.4194	0.1492	93

Sulphuric acid tests were then made with acid of the strength of 0.5 per cent by weight. The results obtained after 53 days' exposure were as given in Table V.

Alternate wet and dry tests were carried out in a large iron thermostat, of the dimensions and shape

shown in Fig. 2, the metal disks being laid, as before, in a circle flatwise on a sheet of paraffin wax. Water entered slowly by tube A, and being admitted to the center of the apparatus, affected all the disks equally. The paraffin disk was perforated by numerous small holes, and rested on a similarly perforated iron disk to enable it to bear the weight of the steels. When the water reached the level B, it was quickly siphoned off automatically by BC, and the level fell to D. It then began to fill again. In this way the metal disks were

TABLE V.—CORROSION OF STEELS IN 0.5 PER CENT SULPHURIC ACID.

Steel No.	Nickel per cent.	Chromium per cent.	Original Weight, grammes.	Loss in Weight, grammes.	Corrosion factor.
1	..	..	34.4266	0.9608	100
2	..	..	36.6388	2.4878	259
3	3.72	..	32.1346	0.5308	55
4	6.14	..	31.9370	0.6042	63
5	26.24	..	31.9886	0.0770	8
6	..	1.12	28.8042	2.1420	223
7	..	3.58	28.9772	0.5830	61
8	..	5.30	30.6176	0.7514	78
9	3.4	1.00	30.9126	1.2722	132
10	3.5	1.12	33.6036	3.9672	413

exposed to alternate wet and dry, the process of filling the thermostat requiring two hours each time. A loosely fitting cover was placed on the top to keep out dust, and to maintain darkness within, in order to prevent, as before, any irregularity of corrosion consequent upon unequal illumination. The results obtained after an exposure extending over 52 days were as given in Table VI.

TABLE VI.—CORROSION OF STEELS ALTERNATELY WET AND DRY.

Steel No.	Nickel per cent.	Chromium per cent.	Original Weight, grammes.	Loss in Weight, grammes.	Corrosion factor.
1	..	..	38.5536	0.2706	100
2	..	..	38.7170	0.2720	100
3	3.72	..	28.3870	0.1165	43
4	6.14	..	31.8660	0.0985	36
5	26.24	..	30.8160	0.0220	8
6	..	1.12	28.5846	0.2512	93
7	..	3.58	28.3886	0.0806	30
8	..	5.30	30.8406	0.0556	21
9	3.4	1.0	29.8748	0.1274	47
10	3.5	1.12	32.7956	0.1404	52

ACCELERATED CORROSION UNRELIABLE.

Acceleration tests as usually carried out with sulphuric acid, yield very misleading results as to the general corrodibility of the metals tested. Thus, for example, the two standard steels corroded at almost identical rates when exposed to faucet water, sea water, wet and dry, and to 0.05 per cent sulphuric acid. But in the 0.5 per cent acid the second steel corroded some two and a half times as rapidly as the first. Very similar discrepancies occur with steels Nos. 6, 9 and 10, the last named corroding more than three times as much as steel No. 9, although in the other tests the two steels behaved similarly, as we should expect from their analogous compositions.

These observations are in perfect harmony with those of Frazer, who found that while samples of basic and acid steel of analogous composition corroded at practically identical rates under ordinary conditions, yet when exposed to the action of the dilute sulphuric acid the results were most irregular, in one case the

acid steel corroding five times as rapidly as the basic steel. The results of the Corrosion Committee of the British Association emphasize the same fact, and C. M. Chapman, working in America, has been led to similar conclusions.

RESULTS OF THE TESTS.

In neutral corroding media the resistance offered to corrosion apparently rises with the percentage of chromium. This is particularly the case for salt water, and the employment of chromium steels in the construction of ships would appear to be fully justified on this ground alone.

Nickel steels appear to be resistant to acid and neutral corroding media alike, the resistivity increasing with the percentage of nickel. The permanence of the 26 per cent nickel steel towards 0.5 per cent acid is particularly noteworthy.

The corrosion factor does not appear to be a purely additive quantity. Thus, for example, in exposure tests with faucet water, the corrosion factors of steels Nos. 3 and 6 respectively are 83 and 85. We might expect, therefore, that since the 3.72 per cent of nickel and the 1.12 per cent of chromium each separately yield the same protection, by having both together in the steel, the same result should accrue as by either doubling the nickel or the chromium content alone. This, however, is not the case, as is evident from a consideration of the results obtained with steels Nos. 4, 7, 9 and 10. Similar conclusions are arrived at from the sea water, and other tests with the same steels.

THE CORROSION ZONE.

When a plate of iron is suspended in stationary water, the surface of which water has free access to the air, the layers of water in contact with the metal yield up their dissolved oxygen and thereby induce corrosion. Fresh supplies of oxygen from the surrounding layers of water now diffuse towards the metal, and in the course of a few hours an equilibrium is set up, the amount of oxygen diffusing towards the metal being exactly equal to that absorbed in producing rust. [A number of tests in proof of the contention were described.]

In order to obtain trustworthy results for the relative corrosions of various irons and steels by immersion in still liquids in troughs, the plates must be suspended considerably further apart than has hitherto been customary. With painted, galvanized, and tinned plates, of course the case is quite different, for, owing to the slow rate of corrosion, the corrosion zone is correspondingly reduced and the plates may be much nearer together. In moving water, likewise, the plates may be nearer, but in both of these cases it is better not to have them too close together, or films of dust may spread from plate to plate and thus galvanically connect them and induce serious corrosion.

INFLUENCE OF LIGHT ON CORROSION.

In the above experiments the troughs were kept in the dark during the periods of exposing the plates, in order to prevent the disturbing influences of unequal

illumination. In actual practice the influence exerted by suspending two plates close together would be even greater than that indicated in the above experiments, since one plate would cast a shadow on the other and thus withdraw from it the stimulating action of light.

Light accelerates corrosion in one or both of two ways: 1. By accelerating the initial stage of corrosion, namely, the oxidation of the metal to the ferrous condition. 2. By accelerating the second stage of corrosion, namely, the oxidation of the ferrous iron to ferric (rust).

As time goes on the accumulation of rust and ferrous oxide becomes so thick that light cannot easily penetrate, and the corrosion proceeds as if the metal were in the dark. Hence the reaction slows up, and the percentage of ferrous iron in the rust begins to fall. This accounts for the relatively small quantities of ferrous iron found in thick rust deposits, even when metallic iron still remains. When all the iron has been oxidized, of course the ferrous oxide slowly follows suit, until even the last traces may be oxidized. There can be little doubt that numerous other factors, such as galvanic action, temperature, nature of the corroding medium, etc., will affect the relative proportions of ferrous and ferric oxide produced during the corrosion of iron.

INFLUENCE OF CARBON ON CORROSION.

A series of practically pure iron-carbon steels were prepared. Bars of each steel were subjected to typical heat treatments, and their relative corrodibilities and other properties have been investigated in each of these various states of heat treatment. By these means, not only was the influence exerted on these properties by variations in carbon percentage determined, but also the influence of variations in the chemical and physical condition in which the carbon exists in these alloys, within the range of commercial treatments.

Test-bars, $4\frac{1}{2}$ in. long by $\frac{3}{8}$ in. diameter, were prepared from each steel in all states of treatment. After polishing, the bars were accurately weighed, immersed in pure ether for at least an hour to remove all grease, dried in a vacuum desiccator, and then suspended in 700 c. c. of filtered sea water. After 91 days' immersion, the bars were taken out, well washed, cleaned with chamois leather until all adherent deposits were removed, dried thoroughly, and weighed again. The bars were then reimmersed in the same jars and sea water as before, for a further period of 75 days, cleaned thoroughly again and reweighed.

SUMMARY OF RESULTS.

Influence of Carbon on Corrodibility.—(a) In rolled, normalized, and annealed steels the corrodibility rises with carbon contents to a maximum at saturation point (0.89 per cent carbon), and falls with further increase of carbon beyond this point. (b) In quenched and tempered steels a continuous rise in corrodibility occurs, with increase of carbon within the range investigated (up to 0.96 per cent carbon), no maximum

corrodibility at saturation point being found in these steels.

Influence of Treatment on Corrodibility.—Quenching increases the corrodibility to a maximum; annealing tends to reduce it to a minimum; while normalizing gives intermediate values. The influence of tempering varies with the tempering temperature.

Factors Determining Corrodibility.—The electromotive forces between the pearlite and ferrite, and between the components of the pearlite itself, are the principal factors determining the corrodibility of unsaturated pearlitic steels above 0.4 per cent carbon. In mild structural steels, the galvanic action, due to differences of potential between the constituents, is accompanied by galvanic action between the ferrite crystals themselves. These differences of electro-potential between the ferrite crystals are the result of differences in their orientation. The state of division of the pearlite, and the presence of internal stresses in the steel, may also exert a considerable modifying influence on the foregoing factors.

The influence of time on the rate of corrosion varies with different steels. In a low-carbon steel it is shown to be practically directed proportional to the length of immersion.

Three per cent of tungsten produces practically no change in the corrodibility of carbon steels.

Decarbonization increases the resistance to corrosion.

The two oxides, FeO and Fe₃O₄ (mill scale), both exert a microscopical pitting effect on steel when in contact with it in sea water.

The value of the production of gold, silver, copper, lead, and zinc in Virginia in 1911, according to H. D. McCaskey of the United States Geological Survey was \$169,394, an increase of \$73,243 over the corresponding value for 1910. Separate figures for the production of copper, lead, and zinc cannot be given without disclosing individual production. The total production of the above metals in Virginia and New York in 1911 was 148.22 fine ounces of gold valued at \$3,064, 21 fine ounces of silver valued at \$11, 90,000 pounds of copper valued at \$11,250, 834,748 pounds of lead valued at \$37,563, and 2,226,658 pounds of zinc (figured as spelter) valued at \$126,920. A small quantity of lead and some zinc ores were shipped from mines in St. Lawrence County, New York. The gold and silver produced came entirely from Virginia and was 105.26 fine ounces in quantity and \$2,176 in value more than in 1910. Of the gold produced 39.09 fine ounces were derived from placers and 109.13 ounces from siliceous ores. Seven fine ounces of the silver came from deep mines and 14 ounces from siliceous ores. There were 13 producing mines in Virginia, of which 5 were placers. The total ore output of Virginia and New York was 18,465 tons, of which 1,761 tons were gold quartz ore from Virginia with an average extraction value in gold and silver of \$1.29 per ton.

QUICKSILVER.

By THOMAS OSBORNE.

Quicksilver occurs in nature principally as a sulphide, occasionally associated to a small extent with the native metal. The compounds of quicksilver with chlorine, selenium, tellurium, antimony are all rare minerals, probably the result of secondary concentrations. The world's supply is obtained from six countries only, the main output about a third, coming from the Almaden mines in Spain. During recent years it has been as follows (see Table I) in metric tons of 2,204.6 lbs.:

	1911.	1910.	1909.	1908.	1907.	1906.	1905.	1904.
Spain	1,055	1,000	1,000	1,065	1,210	1,567	853	1,130
United States...	742	700	717	670	734	890	1,036	1,188
Italy	815	800	700	680	423	418	369	357
Austria	685	694	609	630	610	577	570	550
Mexico	95	200	200	200	200	200	190	190
Russia	27	4	7	49	130	210	318	332
Totals	3,419	3,398	3,233	3,294	3,307	3,862	3,336	3,747

These totals show a very constant output for many years past of the total world's supply. The notable features being a constant increase of the Italian supply and some falling off of that of the United States and Mexico, and a remarkable dwindling of the Russian output. The supply from Austria also tends to increase. Among the practical uses to which quicksilver is now put may be mentioned gold milling; for placer mining; for the manufacture of vermilion; for the supply of fulminates; physical instrument makers use large quantities; it is also required for drugs and lighting. The use of quicksilver for the production of fulminate for percussion caps for igniting powder is increasing in importance probably more rapidly than any other. The chief source of quicksilver has been for many years the well known mines of Almaden belonging to the Spanish Government, which usually makes a contract for the sale of the produce for a period of years—generally ten. Public tenders were asked for last autumn. The terms include the payment of a commission of $1\frac{1}{4}$ per cent on the gross selling price of the quicksilver and of 10 per cent on any excess of price beyond \$39.42 per bottle. This 10 per cent may be a valuable consideration, for the price of quicksilver is generally in excess of that amount. The present price in London is \$40.20.

In the United States there are at present 22 mines producing quicksilver, 19 of which are in California. An increase of three over 1910, when there were 15 in California, two in Nevada and two in Texas. The total American output during recent years has been as follows in flasks of 75 lbs. each:

1911.....	21,821	1905.....	30,451
1910.....	20,937	1904.....	34,570
1909.....	21,075	1903.....	35,620
1908.....	19,752	1902.....	34,291
1907.....	21,567	1901.....	29,727
1906.....	26,238	1900.....	28,317

A total since 1900 of 324,366 flasks giving a recent yearly average of 27,030. The output of 1908 was the

lowest for half a century. These totals show a falling off, as for six years they have been below the recent average; the decline from 1900 to 1911 being 22 per cent. The drop in the American supply is mainly due to the falling off in the output of mines in Nevada and Texas; those of Oregon, Arizona, Utah and Washington have given out altogether. About 83 per cent of the American output is obtained from California; the main production (over 50 per cent) comes from the New Idria mine. The bulk of the output is required for American use, but there is a surplus, which is exported to Canada and Mexico. The details of the American output are as follows:

FOR THE WHOLE OF THE UNITED STATES.				
	Tons of ore worked up.	Quicksilver in flasks.	Per cent average recovery.	Pounds of mercury per ton. Value.
1911	21,820	..	..	\$1,003,980
1910	123,560	20,600	0.6	958,100
1909	154,500	21,075	0.5	957,800
FOR CALIFORNIA.				
1911	19,131	..	..	\$ 880,217
1910	115,306	15,825	0.5	800,484
1909	144,989	1,387	0.4	730,745
FOR TEXAS.				
1911	2,589	..	..	\$ 118,700
1910	8,220	3,320	1.5	154,413
1909	9,107	4,188	1.7	190,345

The United States is now the third largest producer of quicksilver in the world; up to 1907 it was second; during 1904 the states produced 74 per cent more than Italy; now Italy is the second largest producer. Austria appears to be a dangerous competitor.

Great Britain's trade in quicksilver differs entirely from that of the United States; it does not produce quicksilver, but purchases and distributes it, retaining portion for the home market; the quantities imported, exported and retained are known in the following schedule, most of the import comes from the Almaden mines in Spain:

BRITISH IMPORTS, EXPORTS, AND CONSUMPTION IN FLASKS.			
	Imports.	Exports.	Consumption.
1911.....	46,547	31,438	15,109
1910.....	44,595	24,748	19,847
1909.....	43,163	22,050	21,113
1908.....	43,605	22,348	21,257
1907.....	39,448	29,465	9,983
1906.....	38,823	27,712	11,111
1905.....	34,034	21,330	12,704
1904.....	33,218	27,277	15,941
1903.....	34,886	18,846	16,040
1902.....	33,192	19,519	13,673

The quantities imported and distributed are increasing, the imports of 1911 are 40 per cent greater than those for 1902; English consumption fluctuates considerably, that for 1911 is only $10\frac{1}{2}$ per cent greater than for 1902, consequently the exports show a very large increase.

According to the London Times a new process for the utilization of peat, invented by F. H. Nixon, of London, consists of cutting the turf, after it has been air dried, into corrugated blocks, which are sprayed with petroleum so as to form firelighters. The blocks are subsequently given a coating of highly inflammable materials which also strengthens them and prevents them from breaking easily.

IRON CORROSION INVESTIGATIONS.*

By OLIVER P. WATTS.

In Vol. 8 of the transactions of this society, C. F. Burgess called attention to the remarkable reduction in the corrosion of iron by sulphuric acid, brought about by the addition of a small amount of arsenious oxide to the acid. Later he explained the protective action as follows: "The explanation which has been offered for this phenomenon is that the iron receives, by contact with the solution, an extremely thin coat of arsenic, which resists the action of the acid and protects the underlying metals." He also gave experimental proof that the iron was coated with arsenic.

It has long been known that by dipping clean iron into solutions of suitable composition and concentration thin coatings of gold, silver, platinum, copper and several other metals may be deposited on the iron. It is generally conceded that such coatings are not sufficiently continuous and impervious to protect the underlying metal from corrosion, even though the metal forming the coating may itself be thoroughly resistant to the corrosive agent. Instead of being a protection, such coatings are usually considered to be stimulators of corrosion.

Since all metals which thus deposit upon iron when it is immersed in a solution of the metallic salt are electro-negative to iron, a short-circuited voltaic cell is formed, of which the iron is anode and the metal deposit is the cathode. So long as any iron remains in contact with the electrolyte it would seem, except for certain considerations which will be presented later, that the corrosion of the iron ought to be stimulated by this condition, and that the only way in which such a coating could afford good protection would be by covering the iron completely, so that no electrolyte could come in contact with it.

Speaking of the effect of other metals in contact with iron, W. H. Walker says, "Tin is a metal which, like copper, accelerates the corrosion of iron by aiding in the oxidation of the hydrogen set free by the reaction." M. P. Wood calls attention to the injurious action of metals, "The use of anticorrosive or anti-fouling paints, containing salts of any metal, is attended with the greatest danger to the coated (iron or steel) structure. These pigments are extremely sensitive to the presence of saline elements in moisture, their action being to rapidly dissolve portions of the iron and to deposit the metal which they contain upon the surface of the plates, and these deposits, exciting energetic galvanic action, cause corrosion and pitting to go on with alarming rapidity. Both mercury and copper salts are offenders in this way."

It appears, then, that arsenic is unique among the metals which precipitate themselves upon iron from solution, for arsenic protects iron almost completely from powerful corrosive agents, while the other metals

are generally considered to aggravate corrosion and rusting. The protective action of arsenic cannot be due to any superior power of resisting attack by sulphuric acid, for silver, platinum and gold are even more resistant, and yet accelerate the corrosion of iron. It is evident that these other metals do not form continuous and impervious coatings over the iron, else they would protect it. It is difficult, perhaps even impossible, even with the aid of the electric current, to deposit from solution a thin coating of one metal upon another so perfectly as to protect the underlying metal from corrosion by an acid ordinarily capable of attacking it.

It is almost incredible that a thin, yet perfect and non-porous, metallic coating should be deposited by a process which depends for its operation upon the dissolving of the underlying metal. The protective action of coatings of copper, silver, etc., thus deposited on iron is about as effective as would be expected from a knowledge of their method of formation. They are continually being undermined by the corroding of iron anode at points not yet covered, until the copper or silver becomes detached, to have its place taken by a new coating, and so on, as long as any of the salt of the depositing metal remains in the solution. If the coated metal be removed to an acid, the corrosive action is similar, except that the renewal of the coating can take place only at a rate not greater than that at which the detached metal redissolves in the acid.

WHY ARSENIC PROTECTS IRON SO WELL.

If the coating of arsenic is so porous and imperfect as the action of acids shows the coating of copper, for example, to be, how can the arsenic protect the iron any better than copper does? It occurred to the writer that the explanation lay in a high overvoltage or excess potential of hydrogen on arsenic, and the experiments which follow were undertaken to discover whether this is the explanation of the singular and mysterious protective action of arsenic. If the above explanation is correct, among the metals which deposit upon iron when it is immersed in a solution of their salts those having a high overvoltage for hydrogen should protect iron, and those of very low overvoltage should aggravate corrosion.

If an electrode of platinum coated with platinum-black be immersed in normal sulphuric acid the electrode will be electro-negative to the solution by about 1.14 volts. If now a small but slowly increasing electromotive force be applied between this electrode and an insoluble anode it will be found that the platinized cathode becomes progressively electronegative with regard to the solution. When a certain difference of potential between the cathode and the solution is reached, bubbles of hydrogen begin to appear on the cathode. If a cathode of smooth platinum is used, hydrogen will not appear on this until it has become 0.09 volts more positive than the other cathode was when hydrogen first appeared on it. Similarly zinc must be 0.70 and mercury 0.78 volt more positive

*Paper presented before the American Electrochemical Society, in Boston, Mass. April 18-20.

than the platinum-black before hydrogen appears upon them. This excess of potential required to cause a visible liberation of hydrogen upon a cathode of any particular metal, over the potential required for the liberation of hydrogen upon platinum coated with platinum-black, is known as the overvoltage of hydrogen upon that metal. In Table I are given the single potentials in normal solutions of the sulphates of the metals, and the overvoltage of hydrogen as stated by different observers.

TABLE I.—SINGLE POTENTIALS IN NORMAL SOLUTIONS OF SULPHATES OF THE METAL AND OVERVOLTAGE OF HYDROGEN.

	Single potential.	Overvoltage in —normal sulphuric acid—			In 5 per cent KOH. Nutton
		Caspari.	Foerster.	Harkins.	and Law.
Mercury	—0.98	0.78	0.43	0.74	..
Zinc	+0.524	0.70	..	0.71	0.70
Lead	—0.095	0.64	0.35	0.62	0.57
Tin	—0.085	0.53	0.43	0.55	0.61
Cadmium	+0.162	0.48	0.48	..	0.52
Arsenic	—0.550	..	..	0.39	..
Bismuth	—0.490	..	..	0.38	..
Iron	+0.093	..	..	..	0.15
Copper	—0.515	0.23	0.10	0.25	0.41
Cobalt	—0.019	..	..	0.22	..
Nickel	—0.022	0.21	0.10	0.15	0.37
Silver	—0.947	0.15	..	0.13	..
Platinum	—1.140	0.09	0.07	0.07	..
Gold	—1.356	0.02	0.055	..	..

On the theory that the protection of iron by a deposit of arsenic is due to the high overvoltage of hydrogen on the latter the action would be as follows: Iron dissolves and by so doing deposits arsenic upon the surface of the iron. Since the arsenic is deposited simultaneously with the dissolving of the iron, and only as a result of this dissolving, it is hardly possible that the iron should be perfectly covered by arsenic, but here and there holes will exist, allowing the iron to make contact with the electrolyte. Voltaic cells are thus formed. From the single potentials of iron and of arsenic, +0.093 and —0.550, these cells should have an electromotive force of 0.64 volts, and the corrosion of the iron ought to be very vigorous. It is here that the overvoltage of hydrogen comes in play. The iron is anode and the arsenic cathode, and, just as in any other primary cell with sulphuric acid as electrolyte, hydrogen is deposited on the cathode. But when hydrogen is liberated on arsenic the potential of the latter is raised 0.39 volts higher than —0.277, the potential at which hydrogen is liberated on platinum-black. This would raise the potential of the arsenic to +0.113 volts, or higher than the potential of the iron anode. This means that in our iron-arsenic cell there can be no visible evolution of hydrogen on the arsenic, for before this can occur the potential of the cathode has become equal to that of the anode, and corrosion of the iron ceases; in other words, this particular primary cell polarizes so badly that after a few seconds of action its electromotive force has fallen to zero.

If the above explanation is correct, protection should be afforded by those metals which plate out on iron by immersion, and whose overvoltage for hydrogen is great enough to raise their potentials to at least equal the single potential of iron. The potentials of the following metals are far enough below that of iron

to expect that they will deposit on iron even in moderately strong sulphuric acid: Antimony, arsenic, bismuth, gold, lead, mercury, platinum, silver and tin. Potential measurements made by students in the writer's laboratory indicate that chromium should be included in the list. Omitting lead, on account of the insolubility of its sulphate, mercury, tin and arsenic show the highest overvoltage; compounds of these metals were therefore used in a preliminary experiment by A. C. Shape.

[Results of a number of tests are here given in which pieces of No. 22 mild sheet steel, 5 centimeters square, were pickled in sulphuric acid to remove the scale, dried, weighed and corroded in sulphuric acid to which three volumes of water had been added. Reagents were then added to test the protection given by tin, arsenic, mercury, chrome, antimony, bismuth, copper.]

From the experiments given, certain definite conclusions can be drawn and other generalizations now appear probable, but may require revision or rejection in the light of future experiments.

The writer's hypothesis, that the protective action of arsenic is due to its high overvoltage, has been in a general way confirmed. Other metals of high overvoltage have had a protective influence, while all metals of low overvoltage which deposit on iron are accelerators of its corrosion. So far as overvoltages are known, bismuth alone fails to conform to the hypothesis. Theoretically it should retard corrosion; actually it is an accelerator. Unless redeterminations of the overvoltage of bismuth and the single potential of iron shall reconcile theory with fact, the writer's hypothesis fails. The overvoltage of bismuth was presumably measured on a solid electrode. Bismuth deposited as a powder. If there is the same difference in overvoltage for bismuth as between smooth and spongy platinum, this correction would put bismuth in the list of accelerators.

The statements which follow are intended to apply only to the corrosion of iron by sulphuric acid. Tin, chromium and mercury retard corrosion; of these, tin alone is as effective as arsenic. The protective action of mercury is very slight. Oxidizing agents are in themselves accelerators of corrosion by acids, although in dilute solution this may be masked by a protective action which supervenes when the oxygen has been used up, as might happen with chromates.

Reducing agents should show more or less protective action, but this fact remains to be confirmed by further experiment.

In general, the whole subject as here presented is but a preliminary study which opens many possibilities for future investigation.

Austria-Hungary imported in 1911 raw cotton to the amount of 425,050,000 lbs., or about 850,000 bales of 500 lbs. each. Of this 240,850,000 lbs. came from the United States.

SINTERING AND BRIQUETTING FLUE-DUST.*

BY FELIX A. VOGEL, NEW YORK, N. Y.

With the increasing use of fine ores, larger furnaces and high-pressure blast, the production of flue-dust is constantly increasing, and amounts annually in the United States to 3,000,000 to 3,500,000 tons, an exceedingly high tonnage, of which a large part has been discarded as valueless. It is generally a fine material containing considerable coke and iron ore, with a small admixture of lime and silica, depending upon the burden. The iron ore is partly reduced, which shows that it originates largely from the reducing zone of the blast furnace. In the United States the dust usually contains 20 per cent of coke and more than 40 per cent of iron. Estimating coke to be worth \$3.25 per ton, and iron ore 7 cents per unit, a ton of flue-dust, unless made available, represents a loss to the furnaceman of \$3.50 per ton. This accounts for the first efforts to recharge the flue-dust into the furnace, either by moistening it down with an excess of water, or mixing it with clay to form balls or pulp, or treating it with lime water.

To recover, in the blast furnace, all the values represented by the material contained in the flue-dust, the following conditions should be complied with:

1. The dust should be agglomerated into lumps about the size of furnace coke, so that it will help to carry the burden and facilitate the flow of the gases.
2. The agglomerated material should be strong enough to carry the burden without disintegrating; it should be heavy so as to decrease its volume, and it should be sufficiently porous to permit the furnace gases to penetrate fully. Under no condition should the surface be glazed.
3. It should contain all of the valuable constituents of the dust, such as coke, iron ore, lime, etc.
4. It must stand handling, without undue breakage, and should not produce more than 5 per cent of dust.
5. It must stand the weather.
6. It must not disintegrate in the blast furnace before being greatly or totally reduced.
7. It must submit to easy reduction without requiring additional fuel.
8. It must not contain substances detrimental to blast furnace operations.
9. Its cost of production must be low.

Blast furnace operations, by the use of such agglomerated material, will result in: (1) Regular steady operation; (2) Increased burden, increase in the yield and metal produced; (3) Decrease in the consumption of coke; (4) Decrease in the production of flue-dust; (5) Decrease in the cost of producing pig iron.

A number of processes have been evolved in the United States, generally known as agglomerating and sintering processes. They are based on fritting to-

gether the particles of ore by heat, the binding action being due to the formation of silicates, mostly of iron. When the coke has not been eliminated mechanically from the dust, it is burned out, leaving ashes in the agglomerated material, which increases the formation of silicates of iron or glazing material. In some cases, however, more fuel is added to the flue-dust, which, naturally, further increases this drawback.

The nodulizing process, the oldest process in the United States, has been in successful operation for a number of years. Flue-dust is treated either directly, or it is previously submitted to a magnetic separation to eliminate coke and lime. This is done to facilitate the subsequent nodulizing operation, which is carried on in a slowly rotating cement kiln from 80 to 120 ft. long. From 200 to 300 lbs. of finely powdered coal is used per ton of finished material, the coal being blown into the kiln. Gas and oil have also been tried with more or less success. The heat produced is considerable and difficult to control, the semi-soft material formed consisting of iron ore particles and slag, which, by the revolving action of the kiln, is balled together in nodules of various sizes—from a pinhead to that of a cannon ball—which are usually quite dense, often fused and glazed. They contain 60 to 67 per cent of iron, which makes them quite attractive from the furnaceman's point of view. To make nodules an elaborate and expensive plant is required, the operation of which is more or less difficult and costly.

The Huntington-Heberlein pot process, which has been used with good results in the roasting of pyrites cinders, has been recommended for the fritting of flue-dust. The resulting fritted material is of more or less cellular structure. However, this would not be an advantage, as the surface would be largely glazed, rendering it not permeable to gases, and would have to be removed in the blast furnace at about smelting heat. The process is somewhat simple, requiring stationary iron pots fitted with a perforated false bottom through which the air is blown into the charge. The equipment is cheap; the operation, however, is not continuous, which makes it expensive.

The Groendal briquetting process has also been applied to flue-dust. The flue-dust, either moistened, or after the elimination of the coke and stone, is pressed into bricks which are subsequently fritted in high temperature. To facilitate the operation it was found necessary to eliminate the coke; this, however, increases the cost. The separated coke is of little value, since it contains many impurities. The presses used are ordinary brick presses. The bricks are carefully placed in layers on cars, which are run into long kilns about 170 ft. long, where they are submitted to high temperature, gas being used for the purpose. The platforms of the cars are built of fire brick and form the bottom of the kiln. The highest temperature, about 1,300° or 1,400° C., is reached in the center of the kiln, the highly burned briquettes working gradually towards the cooler end of the kiln, where they are finally unloaded. The

*From paper presented at the recent meeting of the American Institute of Mining Engineers.

operation lasts about 7 hours. The resultant briquettes contain from 65 to 70 per cent of iron with practically no impurities, these having been eliminated. No ashes are left by the fuel. The briquettes are only slightly fritted, are very porous and friable, and make a high-class material for use in an open-hearth furnace. The manufacturing of Groendal briquettes is expensive, necessitating a costly plant, which has limited output. A ton of flue-dust will produce about two-thirds of its weight in briquettes.

Quite recently the Dwight-Lloyd process has been applied to the sintering of flue-dust. The material is submitted to internal combustion in layers of from 5 to 7 in. thick. It is fed on an endless conveyor formed of iron pallets or grates. After the fuel therein contained has been ignited by means of a gasolene torch, or some other device, the air is drawn through by suction. The operation lasts about 20 minutes. A good deal has been published of late in regard to this process. It is claimed that the required plant is not costly, while the operating expenses are considerably lower than in the previous process. The resultant sintered material is not homogeneous and, while a large portion of it is of cellular structure, it is glazed on the surface, which makes it quite difficult to reduce in the blast furnace.

The Greenawalt process uses much the same apparatus as the Heberlein pot, but air is drawn through the charge similar to the Dwight-Lloyd process. The sintered material from these various processes is expensive on account of the loss of carbon and, with the exception of the Groendal briquette, is not of good physical structure and is usually glazed on the surface.

The briquetting of flue-dust has been more attractive abroad than has the sintering. The lime process mixes the flue-dust with from 5 to 10 per cent of hydrate of lime and, after briquetting, the material is exposed to the air for a certain length of time, so that a carbonate is formed which is the binding medium. This binder will eventually act as flux and replace a certain amount of stone. The process, while having decided advantages, is quite cumbersome and costly, as the briquettes must dry from two to four weeks under cover.

The pioneer process uses sulphide pitch (obtained from the sulphide pulp mills) as a binder. It is an organic substance, rich in carbon and hydrocarbons, which will burn readily and thus increase the calorific value of the material. The flue-dust is pressed into briquettes with 4 to 8 per cent of sulphide pitch; they are quite hard and give fair results, but the process is expensive.

The Ronay process does not use a binder. The flue-dust is submitted to a very high pressure in a specially constructed type of hydraulic press; the resulting briquettes can be handled immediately and have proved very satisfactory. The process requires an expensive plant, however, increasing the operating cost.

[The Schumacher process does not use what may

properly be called a binder, but is based on the latent cementing actions existing in fresh flue-dust and which are made active by the presence of a small amount of catalytic substance. Thus 0.25 per cent of magnesium chloride mixed with fresh flue-dust and 6 to 10 per cent of water, pressed into briquettes, will create a strong reaction, noticeable by the considerable heat developed; the briquettes will be perfectly set and hard within a few hours. The process is very simple, an ordinary pug mill being used in which to mix the material, which is subsequently pressed into briquettes in a toggle press and then loaded on cars to allow them to set. Some flue-dust will react so strongly that a large amount of ore or coke breeze may be added to the briquettes; in these cases the flue-dust acts as a binder.

The Schumacher process requires an inexpensive plant and the cost of manufacturing is low. It is extensively used abroad and has replaced some of the other methods. The briquettes of all-agglomerated materials have given most satisfactory results abroad and highest returns and values to the blast furnace operators.

IRON AND STEEL BRIQUETS IN FOUNDRY PRACTICE.*

The last few years have seen a remarkable increase in the use of iron and steel briquets in foundry work, and it may not be out of place at this time to make a short review of the work accomplished in this direction and see where the advantage of briquet use comes in.

At first there was a good deal of trouble when using briquets, due mainly to the fact that there was no efficient way of making them and holding them together in the cupolas after charging. This disadvantage has, however, been eliminated with the advance of the briquetting industry and may now be regarded as settled.

The waste for briquets is very low, usually only 3.5 to 5 per cent. At the upper zone of the cupola where the briquets in their red hot state allow the air to pass through, we get that chemical change which gives to briquetted iron the characteristic properties of such treatment.

The graphite burns and a large percentage of silicon is lost, which may go as high as 25 per cent of the entire silicon percentage in the briquets. The briquets also absorb a little more sulphur than is absorbed by the usual charging material, owing to their loose structure.

If these factors are considered in figuring charges, it is very easy to control them for the casings to be poured. Both the decrease in the carbon and silicon percentage, as also the increase in the sulphur percentage, tend to make the casting hard, and will make it very useful for cylinders, although useless for the ordinary machine casting or thin-walled pipes and castings.

*From Castings.

It is then the rule, when making cylinder castings, to use more of the briquets than would be used when making the ordinary machine casting. With cylinder castings between 20 to 30 per cent briquets can be added to the cupola charge, while the ordinary machine castings should never have more than 10 per cent added.

It is impossible to set down a general rule for the use of briquets, but computations should always consider that castings made with briquetted charges will have as a rule 0.2 to 0.3 per cent more silicon than the usual mixture.

Large plants having their own foundries are often confronted by the question whether to use their own chips and metal waste exclusively for briquetting, or whether to use the waste from other plants. Originally most foundries held tenaciously to the former practice, fearing to use metal from a foreign source. Within late years, however, this practice has been gradually abandoned and most foundries buy up chips from sources other than their own plant to use in briquetting. An added safeguard lies in the analysis of the briquets which will give the foundryman an accurate knowledge of the constituents in the same.

Another question which has been discussed for some time is the time of charging briquets. Some claim that they ought to be charged at the beginning of the heat, and some at the end. The best practice seems to charge them near the end of the heat. The briquets are, after all, less solid in structure than the other iron charges and waste castings, and are more liable to break if dropped too great a height. Charging them near the end of the heat safeguards them against breaking through falling too low. In addition to this fact, they are protected against breaking from being struck subsequently by the charging of additional coke or iron charges.

The next question is that of production of these briquets. Long and tedious experiments have been made with briquets, and the latest process, the Ronay process, seems to have solved the problem. This process manufactures briquets without the use of any bonding agent. Large plants have been established in Germany, which make briquets for various foundries, using their scrap metal and making the briquets as per orders. A short description of the production of these briquets may not be without interest.

To have the finished briquets of the right composition it is necessary to make a careful analysis of the chips as they enter the works and then mix the material as needed. Where ordinary machine casting scrap is used a general analysis is sufficient. Where special casting scrap is used, as for example chips from cylinders, rollers, etc., a more careful analysis must be made, and the briquets must be made separately to obtain the right composition.

After analysis the scrap is dumped into bunkers and is conveyed from there by belt conveyers to an exhauster, where they are cleaned of the lighter dust

particles. From there they pass over a magnetic separator, which cleans the scrap still further, and then to the elevator and into the feed of the press. If the chips are in form of long steel chips, or turnings from lathes and other machines, they are first broken in suitable breakers or crushers. Metal chips which must be treated with much greater care, as regards weight and relative composition, are usually delivered to the works in definite weight barrels. As they are usually free of dust particles and impurities they need not be cleaned any further unless it be to place them into centrifugals and thus free them of the oil particles clinging to the chips.

The next step is the pressing of the briquets by means of hydraulic presses. There are five steps before the briquet is finished; they are: feeding the material into the press, stamping it down solid, pressing the briquets, ejecting the finished briquet, and removing the briquet. The material is fed into the press, stamped down solid by a heavy piston and then brought over one of the die molds, where a movable upper and lower die press the material into the required form.

Another piston then pushes the briquet out of the die mold, moves it aside to a belt conveyer, which transports it to the storage yard or building. Most of the briquets are made in cylindrical form and are made in various sizes, depending on the capacity of the melting furnaces and cupolas.

The regular briquets used in cupolas of 12,000 pounds per hour capacity have a weight of 36 pounds. The specific gravity of the briquets is between 5.2 and 5.5, which makes them solid enough to withstand the ordinary rough handling in transportation and charging.

The introduction of the briquets into foundry operation has been made more certain within the last few years through the regular use of laboratory methods in the foundries. Many of the expensive special pig iron materials that seemed a few years back indispensable for foundry charging have been discarded since the introduction of the briquets. The application of the waste iron and steel chips and scrap has opened a way to greater economy and utilization of home products and has decreased the cost of production considerably.

The very fact that the use of briquets has become so general and has been worked up to such a science that the detail composition of the final casting can be computed and obtained, points to the increased application of briquets in foundry operation.

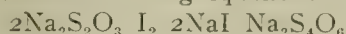
The well known and often described zinc mines at Franklin Furnace, in Sussex County, N. J., continued their important output of metal during 1911, according to the report by H. D. McCaskey, of the U. S. Geological Survey. The New Jersey Zinc Co. treated 306,168 short tons of ore at its concentrating plant and shipped 67,896 tons of crude ore to smelters.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF ARMOUR IN- STITUTE OF TECHNOLOGY.

III.

Iodimetry.—Iodine and sodium thiosulphate react according to the following equation:



The reaction is one of the most rapid and complete of all those used in volumetric analyses, and inasmuch as the iodo starch reaction employed as an indicator is extremely delicate, this reaction lies at the foundation of a number of important and accurate quantitative methods.

Standard solutions of iodine and thiosulphate may be used, in general for two classes of reactions. First, for the oxidation by iodine of such reducing compounds as Na_3AsO_3 , H_2S , SnCl_2 , etc., and second, for the titration, by thiosulphate, of the iodine liberated by oxidizing agents such as $\text{K}_2\text{Cr}_2\text{O}_7$, MnO_2 , KClO_3 , etc.

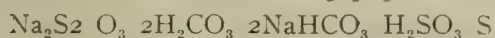
Preparation and Standardization of Solutions.

Ordinarily solutions of tenth normal strength are employed. For the iodine solution, 12.8 grams per litre are weighed out and mixed with 20 grams of potassium iodide.

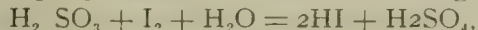
The mixture is triturated in a mortar with water until all is dissolved and the solution diluted to one litre.

Sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, having a molecular weight of 248.3 requires for a litre of N/10 solution about 25 grams. A solution of this strength is prepared, and should be allowed to stand about two weeks before standardization, for the following reason:

Carbonic acid reacts with $\text{Na}_2\text{S}_2\text{O}_3$ as follows:



The H_2SO_3 liberated uses iodine according to

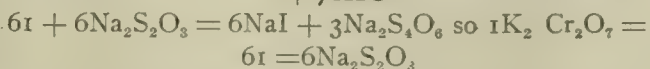
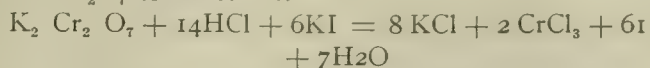


causing the solution to become gradually stronger with respect to iodine. After all of the CO_2 in the water has been used up the thiosulphate solution is practically permanent and may be used for months without restandardization.

Starch indicator is prepared as follows: Half a gm. of starch is mixed with a few cc. of cold water, and to the mixture 100 cc. of boiling water is added. This gives a thin paste, free from lumps or grains. The solution should be made up fresh every few days, but is good so long as its odor shows no decomposition.

The ratio of the iodine and thiosulphate solutions is determined, taking the change from the colorless to the blue iodo starch as the end point.

A variety of substances may be used for standardizing the solutions. The writer prefers the use of $\text{K}_2\text{Cr}_2\text{O}_7$ to all others.



A standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$ is prepared by weighing out exactly 5 grams of the purest salt and making this up to 500 cc. 20 cc. of this (equivalent to 0.2 gms.) is added to 3 grams of KI in strong solution and 10 cc. of concentrated HCl. The whole is diluted to 100 cc. and titrated until the iodine color almost disappears, when starch is added and the titration finished.

$$\text{Weight of } \text{Na}_2\text{S}_2\text{O}_3 \text{ used} = \frac{6\text{Na}_2\text{S}_2\text{O}_3}{\text{K}_2\text{Cr}_2\text{O}_7} \times 0.2 =$$

$$0.2 \times \frac{949.8}{490.3} \text{ and this weight divided by the volume of}$$

solution gives the standard. From the standard of the $\text{Na}_2\text{S}_2\text{O}_3$ that of the iodine solution is calculated.

If a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ standardized by iron is at hand, it may be conveniently used as above, knowing that as $1\text{K}_2\text{Cr}_2\text{O}_7 = 6\text{I} = 6\text{Na}_2\text{S}_2\text{O}_3$ and $1\text{K}_2\text{Cr}_2\text{O}_7 = 6\text{Fe}$, then $1\text{Na}_2\text{S}_2\text{O}_3 = 6\text{Fe}$.

A good sample of "analyzed" $\text{K}_2\text{Cr}_2\text{O}_7$ gives practically identical results when weighed out direct and when standardized by iron.

It should be noted that the reduction of $\text{K}_2\text{Cr}_2\text{O}_7$ gives Cr_2Cl_3 which yields a pale green solution. This will cause no trouble with the end point if the solution is dilute.

A standard KMnO_4 solution may be used in exactly the same manner as the bichromate, the reactions being $2\text{KMnO}_4 + 10\text{KI} + 16\text{HCl} = 12\text{KCl} + 2\text{MnCl}_2 + 8\text{H}_2\text{O} + 10\text{I}$. Therefore $2\text{KMnO}_4 = 10\text{Fe} = 10\text{Na}_2\text{S}_2\text{O}_3$.

The direct standardization of iodine solution by arsenious acid is not recommended.

Iodometric Determinations.—The Bunsen method for oxidizing agents.

In general, any substance which liberates chlorine from hydrochloric acid may be accurately determined by this method. Those ordinarily so analyzed are: pyrolusite for MnO_2 , lead dioxide and its mixtures, red lead, chromates, chlorates, etc.

The apparatus used by the writer is shown in the cut Fig. 1.

A is a large cylinder in which cold water is freely circulated. B is a large test tube containing 100 cc. of KI solution (5% KI). C is a flask fitted with a ground glass stoppered tube. Small samples (0.1 to 0.2 gm.) are weighed out into the flask C, and 10 to 20 cc. of dilute (general 1-1) HCl added. The contents of the flask are then boiled slowly until about half has passed over, and then while still boiling, the connection at D is broken, as the entire flask is lifted clear of the solution of KI, after which the test tube containing the KI and liberated iodine is rinsed out into a large beaker, the solution diluted and the liberated iodine titrated.

When such things as chlorates, or chromates are determined, the HCl added to them should be more dilute than for pyrolusite and similar bodies.

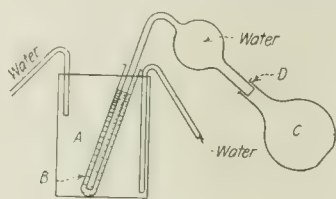
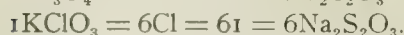
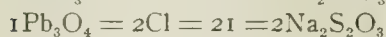
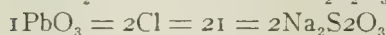
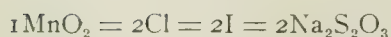
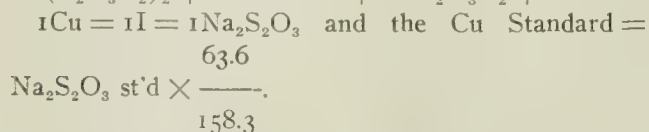
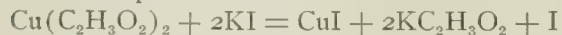


Fig. 1.



Oxidizing agents such as bleaching powder, iodides, bromates, etc., may be analyzed iodometrically in the presence of HCl without previous distillation, in a manner entirely similar to the standardization by means of $\text{K}_2\text{Cr}_2\text{O}_7$.

The Iodimetric Determination of Copper.—Cupric acetate reacts with KI in the presence of acetic acid giving a complete precipitation of cuprous iodide and a liberation of iodine. The iodine, chemically equivalent to the copper present, may be titrated by standard thiosulphate solution.



The copper ore (0.5 grams samples) is decomposed by 5 cc. HCl + 3 cc. HNO_3 , followed by 5 cc. H_2SO_4 , and the whole evaporated to copious fumes of SO_3 .

The mass after cooling is taken up with water and filtered. The solution is then boiled until colorless with two pieces of aluminum foil, when 25 cc. of H_2S water is added and whole filtered and washed with H_2S water. The filtrate should not be brown. The mixture of Cu and CuS on the filter paper and adhering to the aluminum is dissolved in the least possible quantity of dilute nitric acid, the acid being poured through the paper into the beaker and the paper washed. It is often convenient to keep the bulk of the

precipitate in the beaker, washing by decantation. To the solution of copper nitrate, bromine water is added to a brown coloration and the whole boiled to the complete elimination of bromine. This assures the decomposition of H_2S , which would otherwise use up iodine in the subsequent operations. To the solution free from H_2S and Br, ammonia is added in slight excess, and the excess removed by boiling when the whole is acidified by acetic acid, cooled, diluted and 2 grams of KI added. After standing a few moments the liberated iodine is titrated to the disappearance of the blue iodo starch.

The end point is not entirely permanent but the blue color should not return for several minutes.

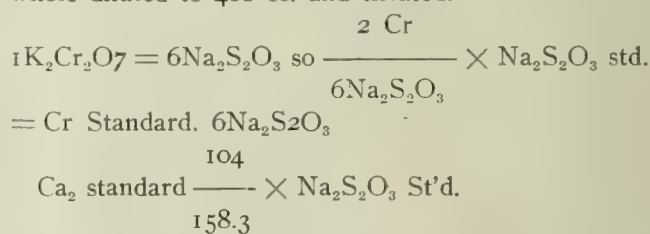
The paper by Sagiura and Kobey in this issue of the Chemical Engineer should be read in this connection.

For copper alloys such as brass and bronze, iron being absent, the precipitation of the copper by aluminum may be omitted, the sulphate solution being treated with ammonia, the ammonia boiled off and acetic acid added and the determination completed.

It is sometimes convenient to standardize the thio-sulphate solution directly against copper. In this case, standard copper foil is treated just as the precipitated copper in the method given above, the treatment with bromine being of course omitted. Large excess of nitric acid, and also of acetic acid must be avoided.

The determination of Chromium in Chromite.

The 0.5 gram sample of chrome ore is decomposed by fusion with 2 to 4 grams of Na_2O_2 in a nickel crucible over a small flame. This oxidizes the Cr_2O_3 present to Na_2CrO_4 . The resulting fusion is extracted by water and the gangue, the ferric oxide, nickel oxide from the crucible, etc., filtered off. The solution is then evaporated nearly to dryness to decompose the last traces of peroxide, taken up in a little water, 2 grams of KI and 10 cc. of HCl added, the whole diluted to 400 cc. and titrated.



Iodimetric methods in general are subject to the following precautions. All titrations and reactions which precede titration should be carried out in solutions which are cold and also dilute. A considerable excess of KI is necessary, not only for the sake of the reaction itself, but also because the end reaction is more delicate in its presence.

The purity of the KI should be known, KIO_3 frequently contaminates it and in that case, a blank experiment should be run and the amount of $\text{Na}_2\text{S}_2\text{O}_3$ solution used per gram of KI determined. This should be very small.

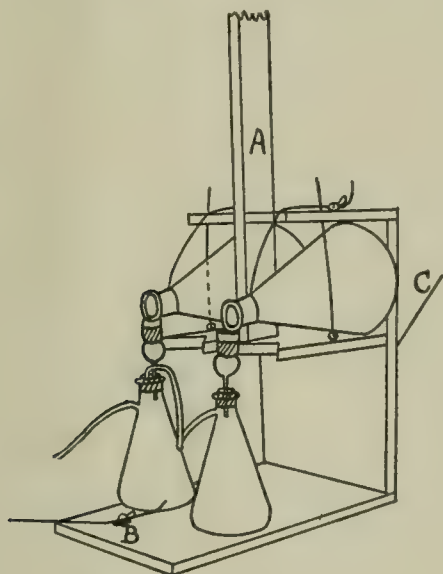
When iodine is titrated, the starch indicator should

not be added until the greater part of the iodine has been used up, as indicated by the fading of the brown or yellow color.

AN AUTOMATIC FILTER.

The apparatus as shown in the accompanying cut has been constructed by E. E. Wallace in the Harvard laboratory. It has been found to operate very satisfactorily in the filtration of the silver haloids through a Munroe-Gooch crucible. The following description of the filter is taken from the Journal by the American Chemical Society:

"The apparatus consists of a wooden framework to hold the bottles, which is suspended by a rigid arm (*A*) 3 ft. long from a horizontal beam by a bolt in such a way as to allow the apparatus to swing with



Sketch of Automatic Filter.

freedom. The suction flasks are held in position by straps to the bottom boards. The precipitation flasks are suspended by wires at the necks so that the lips of the flask sit well into the crucibles, and are kept in position at the sides by stout brass rods. The rods are so arranged that they easily unhook and are loose enough to admit of easy rotation of the precipitation flasks. The frame work containing the bottles is held in position at either end by strong flexible wire, one piece (*C*) leading over a pulley to a heavy weight, the other from the front (*B*) over a pulley to a drum which is attached to the works of a clock, the length of whose pendulum bob is easily adjusted to give a large variation of speed of drum. Clamps of the window sash style have at each point of attachment been used to hold the ends of the wires.

In operation the framework is first swung to the side nearest the clock so that the precipitation flasks are held in an upright position and a slight adjustment of the wire at *B* will start the liquid filtering. If the clock be then started and the pendulum regulated, the apparatus may be safely left, the final position of the flask being such as to drain it completely.

To wash the precipitate, the apparatus is swung to the middle position and the wash water added, the flask shaken and the liquid filtered off in the same manner as already described.

To transfer the precipitates, the crucibles and mouths of the precipitation flasks are lowered, the framework is hooked back so that the flasks incline sharply to the crucible. The precipitate may be taken washed out easily and completely.

The apparatus is believed to have the following advantages: (1) less dust would fall into the analyses; (2) an especially tiresome delay of time avoided; (3) less possibility of the spilling or the overflowing of the crucible while filtering; and (4) two or more filtrations may be conducted simultaneously.

QUALITATIVE DETECTION OF ALKALI BICARBONATES.

In preparing sodium carbonate from sodium bicarbonate for the standardization of acids, it is desirable to have a means of ascertaining whether the bicarbonate is completely decomposed or not. The following test for bicarbonates in the presence of large quantities of normal carbonates was described by R. T. Haslam in the Journal of the American Chemical Society.

The test depends first on the fact that alkali bicarbonates, on the addition of calcium chloride, precipitate CaCO_3 with the liberation of carbon dioxide, and second, that CaCO_3 dissolves somewhat in water containing carbon dioxide with the formation of calcium acid carbonate. If the calcium acid carbonate thus formed is neutralized with ammonium hydroxide, the CaCO_3 is of course reprecipitated.

Dissolve the substance to be tested in water that has been previously boiled to expel the carbon dioxide, and add CaCl_2 in excess. Allow this to stand four or five minutes and filter off the CaCO_3 . Then add a few drops of NH_4OH , and if the substance contained a bicarbonate, a precipitate of CaCO_3 is again obtained. With a large amount of bicarbonate the precipitation will take place in about one-half a minute, while with a very small amount the time required may be eight to ten minutes. However, with no bicarbonate a perfect blank is obtained even after long standing.

This test will detect 0.1 per cent of NaHCO_3 in a normal sodium carbonate. The presence of ammonium salts vitiates the results on account of the solubility of CaCO_3 in such solutions.

The largest item of export from the Birmingham consular district to the United States in 1911 was wood pulp yarn, or artificial silk. This industry was established in Coventry only a few years ago, and its owners have since organized a company and constructed a factory in the United States. The increased exports to the United States, in spite of the production of the yarn there, indicate the extent of the increase in the use of artificial silk.

THE QUANTITATIVE DETERMINATION OF PERCHLORATES.*

By ARTHUR B. LAMB and JOHN W. MARDEN.

In the course of a study of certain cobaltamines it became necessary to make accurate analyses of perchlorates. A study of the literature indicated that no really satisfactory method of analyses had been worked out, and a number of trials by several methods confirmed this conclusion. We finally located the disturbing factor in the simplest of these methods, and by a proper mode of procedure eliminated it altogether, so that now we can determine perchlorate with ease, speed and accuracy.

A fusion method for the analysis of perchlorates, follow by the determination of the chloride formed, would seem to present no special difficulties. As a matter of fact, in spite of many attempts, it appears that no accurate results have heretofore been obtained in this way. Many different fusion mixtures and different methods of procedure have been suggested. The method of Bangley,¹ according to which the perchlorate is ignited with ammonium chloride, has been recommended, but it is admitted that an accuracy greater than 1 per cent cannot be expected. A method described by Carnot² has also been recommended.³ In this method the perchlorate is mixed with sand in a platinum crucible and this is heated to a dull red color. Carnot claimed an accuracy of 0.1 per cent, but in spite of repeated trials we have been unable to approach this accuracy. The results of our last two trials, made with a pure sample of potassium perchlorate, were the best, and are given in Table I:

TABLE I.—ANALYSIS OF POTASSIUM PERCHLORATE BY CARNOT'S METHOD.

No. of expt.	KClO ₄ Wt. taken.	AgCl. Wt. calc.	Blank. Wt. found.	AgCl. Error. Gram.	Error. Per cent.
1	0.4562	0.4720	0.0000	0.4593 —0.0127	—2.69
2	0.4677	0.4805	0.0000	0.4771 —0.0034	—0.70

It will be seen that the errors are very considerable. It appeared in earlier trials as though these errors might be due to a loss by volatilization, and the temperature was therefore kept as low as possible; but this could not be carried too far as there was, on the other hand, the danger of incomplete decomposition due to too low a temperature. There is no sure way by this method of avoiding these alternative difficulties.

Dupré⁴ apparently appreciated these difficulties, for in determining the perchlorates in saltpeter by ignition, he used a platinum crucible surrounded by a specially constructed oven which maintained a constant temperature of 545°. His results appear to be somewhat better than those we have obtained by the Carnot method. The results of the only analyses he publishes, where adequate amounts of perchlorate were used, are given in the following table (Table II):

TABLE II.—ANALYSES OF POTASSIUM PERCHLORATE BY DUPRÉ'S METHOD.

No. of expt.	KClO ₄ Wt. taken.	AgCl. Wt. calc.	Blank. Wt. found.	AgCl. Error. Gram.	Error. Per cent.
1	0.0035	0.995	0.0000	0.986 —0.009	—1.0
2	0.0035	0.498	0.0000	0.492 —0.006	—1.2
3	0.0035	0.249	0.0000	0.250 +0.001	+0.4
4	0.0035	0.099	0.0000	0.099 ±0.000	+0.0
5	0.0035	0.050	0.0000	0.054 +0.004	+8.0
6	0.0035	0.025	0.0000	0.028 +0.003	+12.0

These results are still very unsatisfactory.

A method proposed by Dietrich and Ballenbach⁵ appears to be the most successful modification, so far, of the fusion method. These authors fused the perchlorate with a mixture of potassium nitrate and nitrite. The only results they have published are reproduced in Table III:

TABLE III.—ANALYSES OF POTASSIUM PERCHLORATE BY DIETRICH AND BALLENBACH.

No. of expt.	KClO ₄ Wt. taken.	AgCl. Wt. calc.	Blank. Wt. found.	AgCl. Error. Gram.	Error. Per cent.
1	0.3924	0.4062	0.0000	0.4070 +0.0008	+0.19
2	0.4436	0.4589	0.0000	0.4574 —0.0015	—0.32

Flux added.
KNO₃ and KNO₂
KNO₃ and KNO₂

While better than any of the previously cited results their errors are still considerable.

Influenced by the ill success of these various modifications of the fusion method a number of investigators⁶ have worked out methods of reduction and analysis in solution. One by Rothmund,⁷ using titanium sulfate, appears to be the most successful of them, but while apparently accurate enough, it is long and time consuming when compared with the direct fusion method. It seemed to us worth while, therefore, to locate the source of error in the fusion method and to remove it is possible.

The sign of the errors in all the modifications of this method so far tried has been almost always negative; that is, too little silver chloride has been obtained. Such a result would be caused by either of the two alternatives above mentioned, that is, either by incomplete reduction or by volatilization.

To obtain evidence bearing upon these alternatives we fused samples of pure potassium perchlorate with many different fluxes; with potassium bisulfate and zinc, with sodium carbonate alone, and with sodium carbonate mixed with sodium sulfite or powdered charcoal, or with powdered charcoal and titanium sulfate. It is not necessary to give the results of these fusions in detail. Low results were again obtained in every case, but the error was fairly constant and never amounted to more than 1.0 per cent, even where no reducing agent was present. The fusions with the flux containing sodium carbonate, carbon and titanium sulfate gave the best results, but even they were always from 0.2-0.4 per cent low. The use of a double crucible with a double cover seemed to be only a slight improvement. These experiments indicated that the reducing agent was of little importance and that the

*Read before the Section of Inorganic and Physical Chemistry of the American Chemical Society at the Washington meeting, Dec. 28, 1911.

¹Treadwell and Hall, "Analytical Chem.," Vol. II.

²Compt. rend., 122, 452 (1896).

³Sutton, "Volumetric Analysis," p. 175 (1904).

⁴J. Soc. Chem. Ind., 21, 825 (1902).

⁵Ber., 38, 751 (1905).

⁶Rothmund, Chem. Ztg., 33, 1245 (1909). Sjollema, Z. anorg. Chem., 42, 127 (1904). Kreiden, Z. anorg. Chem., 10, 277 (1895).

⁷Loc. cit.

small discrepancies were probably due not to incomplete reduction but to a slight loss by volatilization.

To test this conclusion a number of fusions were carried on in a glass combustion tube through which a slow current of air was drawn. Plugs of asbestos wool were inserted near the outlet end of the tube, and to this two U-tubes containing beads wet with water were attached in series. The perchlorate with flux was placed in a platinum boat and heated for about twenty minutes. The plugs of asbestos and the moistened beads prevented the escape of any chloride vapor or fumes, for, although the water in the first U tube usually gave a slight test for chlorides after a fusion, no chloride was ever detected in the second U tube. After cooling, the contents of the combustion tube and the U tube were washed upon a platinum gooch filter with hot water, the chloride precipitated, and the silver chloride dried in an electric oven at 170°-180°. Different fusion mixtures were employed; first sodium carbonate mixed with powdered charcoal and titanium sulfate; later the titanium sulfate and then the charcoal too were omitted. Since the charcoal, titanium sulfate and asbestos were all found to contain traces of chlorides, blank determinations were made upon each of them and appropriate corrections, always very small, were applied. The use of warm water in washing resulted in a rapid removal of the silver and potassium nitrate from the precipitate, but according to the measurements of Böttger⁸ and Kohlrausch⁹ must have entailed a slight loss of silver chloride. The temperature of the wash water was about 60° and its total volume, since it was applied in small quantities at a time, amounted only to between 50-75 cc. A saturated solution of silver chloride in pure water of this volume and temperature would have contained about 0.4 mg. of silver chloride, but since the washing was soon discontinued after the wash waters showed no test for silver ions, the first two-thirds of the wash water could have contained only a negligible quantity of silver chloride. The loss of silver chloride then must have been only about 0.1 mg. We have added this almost negligible correction to the observed weights of silver chloride. The results of these experiments are given in Table IV.

These results, with an average deviation from theory of only 0.2 mg. of silver chloride or 0.1 per cent, demonstrate that accurate results can be obtained by the fusion method; that reducing agents are unnecessary and that the low results of previous analyses by the fusion method must have been due to losses by volatilization.

With these points established we resorted to a much simpler and yet equally efficient form of apparatus. It consisted merely of a thin glass (Jena) test tube of 25-30 cc. capacity fitted with two plugs of asbestos wool. The plugs were 15 mm. thick; the first was placed 50 mm., the second 95 mm. from the bottom of the test tube. The perchlorate was weighed directly into the test tube, the plugs inserted, the tube clamped in a nearly horizontal position and the lower end gently heated. White fumes were formed as the oxygen was expelled but these were completely retained by the first plug. When effervescence had ceased, a somewhat larger flame was applied until all the chloride was thoroughly fused. The time required for this heating varies between 10 and 15 minutes. It is a decided advantage to be able to watch the progress of the fusion. After cooling, the contents of the tube were washed upon a filter with warm water, the chloride was precipitated and the silver chloride dried as before. The weights were carefully calibrated and vacuum corrections applied, taking 2.52 and 5.57 as the specific gravities of the potassium perchlorate and the silver chloride, respectively. As before, a correction of 0.1 mg. was applied for the silver chloride dissolved by the warm wash water.

The same sample of potassium perchlorate which was used in the combustion tube fusions was first analyzed by this method. This sample had been found to be free from chlorides, chlorates or sulfates and from other metals than potassium. The results of these analyses are given in Table V:

TABLE V.—ANALYSIS OF SAMPLE NO. 1 POTASSIUM PERCHLORATE BY TEST TUBE METHOD.

No. of expt.	KClO ₄ Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Deviation. Gram.	Deviation. Per cent.
8	0.2290	0.2369	+0.0002	0.2371	±0.0000	±0.00
9	0.3455	0.3574	+0.0002	0.3577	+0.0001	+0.03
10	0.5904	0.6107	+0.0002	0.6107	-0.0002	-0.03

The average deviation from the calculated value in the analyses is but 0.02 per cent.

A second sample of potassium perchlorate was prepared from the above sample by a double recrystallization from redistilled water in Jena glass flasks, using as low temperatures as possible. The resulting 50 gms. of salt was ground and then dried to constant weights at 130° in an electric oven. Analyses made upon it are given in Table VI:

TABLE VI.—ANALYSES OF SAMPLE NO. 2 POTASSIUM PERCHLORATE BY TEST TUBE METHOD.

No. of expt.	KClO ₄ Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Deviation. Gram.	Deviation. Per cent.
11	0.4561	0.4718	+0.0002	0.4720	±0.0000	±0.00
12	0.4437	0.4590	+0.0002	0.4590	-0.0002	-0.04
13	0.4501	0.4656	+0.0002	0.4658	±0.0000	+0.00

These results are practically identical with those

⁸Z. physik. Chem., 46, 603 (1903).

⁹Kohlrausch and Holborn, "Leitvermögen," p. 216.

TABLE IV.—FUSION ANALYSES OF POTASSIUM PERCHLORATE IN A TUBE.

No. of expt.	KClO ₄ Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Deviation. Gram.	Deviation. Per cent.	Flux added.
3	0.2049	0.2119	0.0015	0.2134	±0.0000	±0.00	Na ₂ CO ₃ /Ti(SO ₄) ₂ and C
4	0.2005	0.2074	0.0015	0.2086	-0.0003	-0.15	"
5	0.2506	0.2592	0.0015	0.2603	-0.0004	-0.15	"
6	0.2605	0.2695	0.0010	0.2699	-0.0006	-0.22	Na ₂ CO ₃ and C
7	0.2017	0.2086	0.0002	0.2085	-0.0003	-0.15	Na ₂ CO ₃

obtained with the previous sample and demonstrate the purity of both.

This method was now employed to analyze a newly prepared aquopentammine cobalt perchlorate. It was necessary to dilute the cobaltamine, else a rather explosive decomposition took place; pure sodium nitrate was used for this purpose. The results are given in Table VII:

TABLE VII.—ANALYSES OF AQUOPENTAMMINE COBALT PERCHLORATE BY TEST TUBE METHOD.

No. of expt.	KClO ₄ Wt. taken.	AgCl. Wt. calc.	Blank. Wt. found.	AgCl. Wt. found.	Deviation. Gram.	Deviation. Per cent.
14	0.2900	0.2704	+0.0002	0.2706	±0.0000	±0.00
15	0.3312	0.3121	+0.0002	0.3124	+0.0001	+0.03

They agree nearly as well with the requirements of theory as do the analyses of potassium perchlorate.

The above analyses demonstrate beyond question the accuracy of this method. The average duration from the calculated weight of silver chloride was less than 0.02 per cent, which is certainly equal to the attainable accuracy of the chloride determination itself under these conditions. Moreover, *every* analysis made by this new process has been here recorded. The apparatus is very simple; a hard glass test tube is preferable to an ordinary soft one, but the treatment is not severe. We used the same thin glass test tube for the first three analyses without any perceptible injury to it. The fusion can be easily controlled and the whole analysis requires scarcely more than an ordinary chloride determination. If this latter determination is made volumetrically, the whole analysis becomes a very rapid one.

In conclusion, then, we can present the above as a very accurate, simple and rapid method for the determination of perchlorates.

The abrasive industry in the United States showed a gain in 1911 compared with 1910, according to W. C. Phalen, of the U. S. Geological Survey, in an advance chapter from "Mineral Resources of the United States" for 1911. Though the total value of the abrasive materials entering the trade fell off, the decline was in the importation and not in the domestic production, which increase slightly in value. The value of the natural abrasives produced increased \$119,985, which was more than enough to offset the decrease in the value of the artificial abrasives produced. The fact that the decline in the total figures is attributable chiefly to the falling off in imports is a good indication of an increasingly healthy condition in the domestic industry. The value of the abrasive materials consumed in the United States in 1911 was \$3,725,223, of which \$3,019,803 worth were of domestic production. In the natural-abrasive industry gains were shown in the production of millstones and the quarry products made in connection with them, such as chasers and drag stones, of grinding stones and pulpstones, of abrasive garnet, and of infusorial earth and tripoli. There was a very slight decrease in the

value of the oilstones and scythestones produced and a small decrease in the production of pumice. The greatest decrease was shown in the production of emery. The annual report on abrasives published by the Geological Survey contains from year to year detailed descriptions of the various abrasive industries. The report for 1911 includes a description of the millstone industry in New York and Virginia; the oilstone of Arkansas; garnet milling in New Hampshire, etc. In previous years other branches of the industry have been treated. In this way the entire field is covered every few years and the different chapters thus serve as a contemporary review of the conditions in the industry. The report also includes complete statistics of production of the abrasive materials produced in the United States, together with tables of exports, imports, etc. Natural abrasives were produced in 24 states of the Union in 1911.

So-called "geuine lava tips" are not made from lava, but from talc, with which soapstone is closely allied. The talc and soapstone industry is an important smaller branch of our mineral production. Last year, according to a report by J. S. Diller, of the U. S. Geological Survey, issued as an advance chapter from "Mineral Resources" for 1911, the production was 143,551 short tons, valued at \$1,646,018. This was a decrease in quantity compared with 1910 of 7,165 tons, but an increase in price of \$53,625, due apparently to the sale of a larger proportion of the output in manufactured form. The imports for consumption in 1911 were only 7,550 tons, valued at \$88,288, a decrease of nearly 10 per cent in quantity and of 18 per cent in value compared with the corresponding imports for 1910. With the exception of a small production in California the entire output of talc and soapstone in the United States comes from a comparatively narrow belt of ancient crystalline rocks running through the Atlantic states from Massachusetts and Vermont to Georgia. The producing states are Georgia, Maryland, Massachusetts, New Jersey, New York, North Carolina, Pennsylvania, Rhode Island, Vermont and Virginia. More than 43 per cent of the total output of the United States in 1911 came from New York. The supply of best grades of talc in the United States, such as are used for toilet powders, electric insulators, gas tips, and the like, is not nearly equal to the demand and these grades are imported, chiefly from Italy and France. Talc and soapstone are usually marketed either in rough or crude form from the mine, sawed into slabs, as manufactured articles, or as ground talc. The uses to which they are put include the manufacture of bath and laundry tubs, fire brick for stoves, heaters, etc., hearthstones, mantels, sinks, griddles, slate pencils, gas tips, burner blanks, crayons, and numerous other articles for everyday use, foundry facings, paper, lubricators, for dressing skins and leather, paint, pigment, etc.

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NOTES AND COMMENTS.

Neglected Opportunities.

The field of sewage disposal seems to be one which has been sadly neglected by the chemical engineers. The greater part of the methods now in vogue for the treatment of sewage are chemical, bacteriological or a combination of the two. We find, however, that very few chemical engineers have interested themselves in this subject.

Practically all of our present plants for sewage disposal are designed and constructed by and under the supervision of civil engineers. This may have been good engineering practice when practically the only method of sewage disposal was sewage dispersal. At this time all that was needed in a sewage disposal plant was a determination of the necessary grades and the construction of adequate drains to convey the sewage to the nearest lake or stream. The day for this method of sewage disposal has now passed. It will be a question of only a short time until all sewage discharging into lake or stream must be free from all objectionable material. This is now a requisite in most instances. Where such a condition is required the problem is one which must fall within the field of the chemical engineer rather than that of the civil engineer.

There is also much work which may be done on the part of the chemical engineer to perfect present methods of sewage disposal. There seems to be no insurmountable difficulty in the way of so handling the sewage of a large city, particularly one with many industrial establishments, that valuable material may be recovered from the sewage. Some such plans have already been proposed and a few of them are in operation in a small way.

This will be an undisputed field for the chemical engineer and one which promises very material reward.

Chemical Schedule Revision Bill Prospects in Senate

It now seems likely that the U. S. Senate at its present session will pass the Chemical Schedule Revision Bill. Regarding the prospects of this the Oil Paint and Drug Reporter has the following:

Whether there is to be any serious intention on the part of Congress to get through any of the tariff bills, at least so far as presenting them to the President, the Senate has finally put through the iron and steel schedule revision bill with a number of amendments which are calculated to create a deadlock in conference between the two houses on this schedule. The most notable change is that of repealing the reciprocity act which passed in the special session of Congress, and thereby restoring the duty on print paper, but with a provision in the amendment as is now proposed for making the duty on print paper \$2 a ton instead of \$3.75. This and some other changes in the amendments made by the Senate will be stoutly contested by the House, with the chances that the bill may perish in conference.

The Democratic minority of the Finance Committee, which has charge of the bills in the Senate, on account of the adverse report on all of the bills that have passed the House now propose to take up next the chemical schedule revision bill. This bill is made the unfinished business in the Senate, and may be considered from day to day, with the chances of its passage in some form. This action is a result of the determination of the Democratic minority in the Senate to pass these bills up to the President for his consideration, and the willingness of leaders of the Republican majority in the Senate to allow this privilege to the Democrats. The result of this understanding among the Democratic and Republican leaders is that the tariff bills will probably pass with Democratic majorities as was done, in the case of the steel bill, a sufficient number of the regular Republicans, or high tariff men, abstaining from voting in order to allow the bills to go through with a Democratic majority registered in favor of them. This action may be taken with respect to the chemical bill. Only one of the so-called low tariff insurgent Republicans voted for the Democratic steel bill as it passed the Senate.

All other legislation, including the pure food bill and the pending measure with reference to opium legisla-

tion, is receiving no consideration at this time. The hearings on the subject of the pure food law amendments have not yet been printed, and the Ways and Means Committee shows no disposition at this time to consider the opium bill, which has the support of the government in the effort to carry out the policy agreed upon at The Hague conference. The only possibility for the opium bill to be considered is a continuation of the session of Congress considerably beyond the Presidential conventions during June.

BOOKS RECEIVED.

First Annual Report of Bureau of Mines.

This first annual report of Dr. Holmes, the first director of the new Bureau of Mines, marks what we may hope will be the beginning of a new era with the mining and metallurgical industries of the country.

Those who are most familiar with this phase of our industrial life must certainly admit that the existence of the Bureau is well justified and that in this initial report there is a strong beginning and a high aim to meet the opportunity. We must not infer that there has been no progress in our industries, for we are at this moment in the heat of mining and metallurgical progress and the attainments have been already great. But equally great changes and improvements are before us and no sane man can deny that government help in breaking new ground and by the dissemination of knowledge already gained will be of inestimable benefit.

Much depends on the point of view; we stand with those who are looking forward and for the good that may be attained. Some profess that the zinc mining and smelting industry is already highly perfected and needs little more attention; others say it is the crudest and most backward of any of our metallurgical endeavors, and that 40 years has seen little of real progress in its development. We certainly look to see much accomplishment with this particular metal, both in the amount and manner of saving it.

The same outlook is possible for each and all of our mineral industries, and while not wishing an immediate or complete revolution of the industry, it is safe to expect that the Bureau shall always be a profitable institution, measured in its full significance, and that its success shall be above reproach in the matter of leadership, guidance and the diffusion of information.

To one not acquainted with the conditions it is a little startling that the first year's work, with expenditure of over a half million dollars, has accomplished or considered little beyond fuel investigations and coal mine rescue work. It is explained that the fuel work is the continuation of the endeavors of the Geological Survey, begun in 1904, and on July 1, 1910, transferred to the new Bureau. The continuation of this work and expenditure of an additional \$160,000 for mine rescue work consumed all available funds. The

new and broader field is mentioned and with the excellent personnel already chosen there is little to fear that when sufficient funds are available there will be abundant evidence of results.

The coal mine rescue work is an undertaking imperatively demanded and worthy of the first consideration; it is likewise worthy of attention that the Bureau mentions that the other exigencies of coal mining demand as many lives as explosions, and that the Bureau is already considering them.

It is not difficult to imagine the difficulties and hamperings which beset the efforts of those in governmental employ, we wish to recognize this and also that definite practical results are often slow and difficult to attain in research work; but along certain lines and for various purposes we must expect efficiency. If the Bureau is handicapped for want of mines and facilities it should most plausibly obtain and operate suitable properties. Let the same be operated at a profit, if possible. Work of that sort, embodying the actualities of investigation and improvement and display is the best possible object lesson for our national education. Visible demonstration and wide publicity dispels the last excuse of willful uncompliance, and whips the laggards to meet the conditions of current progress.

The matter of fuel investigations contains its own justification, but one feature is possibly rather disquieting. We refer to the details on page 23 of the report where the statement is made that during the year 56,567 determinations were made on the composition of coal, namely, for moisture, ash, sulphur, volatile matter and heat value. The chemical analyses of the coal samples was made by 14 men, chemists, assistants, etc. Now, it is merely a matter of division to detect that if we allow 300 working days for the year this amounts to some 189 determinations a day; we have, then, 14 men making some 189 determinations per day, let us say an average of 14 per man. Considering the nature of this work, its standardization and simplicity, we are surprised that it could keep half as many men busy.

Quite in line with this criticism is our conclusion that far too much nicety is devoted to the chemical analysis of the coal and too little attention given to obtaining the sample itself. There is certainly little virtue in an accurate analysis of an inaccurate sample. Definite procedure and good judgment may be expended on the collecting of the sample, but our art of sampling is advanced beyond that and our standard now is that the sample itself must be accurate. Full mechanical sampling on coal or on similar material is current practice at various mines and metallurgical works in all parts of the country and it is only trite to state that grab or personally selected samples have other fields of usefulness than in representing the accurate composition of a particular parcel of commodity. Is it too much to expect that the Bureau shall yet develop this line so that suitable plants at

mine or yard or cellar shall handle the whole lot mechanically, thus obtaining a sample worthy of the utmost attention of the chemists? Both the damage done the coal by such treatment and the cost of the work can be made quite insignificant; this appears desirable from our present information as to how the sampling is now accomplished.

As an institution the Bureau of Mines is yet on the threshold of entering its field. Throughout the land greater industry waits for its work to commence; in diffusing the knowledge we already possess the great generality of miners, mill men and smelters have abundance to learn; not less important, setting new standards beyond present reach by scientific work and by research along industrial lines the foremost shall be excelled and all receive benefit thereby.

H. B. PULSIFER.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Bldg., Washington, D. C.:

1,016,803. Manufacture of **Dextrin**. Joseph Verity, Stratford, England, assignor to Carlo Frua De Angeli, Milan, Italy. Patented February 6, 1912.

1,016,804. Manufacture of **Metallic Filaments** for Incandescence Lighting. Christoph Heinrich Weber, Berlin, Germany. Patented February 6, 1912.

1,016,844. Artificial **Tobacco** and Process of Making Same. Adolph Moonelis, New York, N. Y. Patented February 6, 1912.

The process comprises making a tobacco paper of tobacco fiber free of water-soluble constituents and treating such paper with a distilled-water extract of a good grade of tobacco leaves.

1,016,874. Means and Method for Preventing Depletion of **Electrolyte**. Thomas A. Edison, Llewellyn Park, N. J., assignor to Edison Storage Battery Company, West Orange, N. J., a corporation of New Jersey. Patented February 6, 1912.

1,016,989. Process of Utilizing **Lime-Mud** in the Manufacture of Fertilizers. Hugh A. Galt, Barberton, Ohio, assignor to Columbia Chemical Company, Barberton, Ohio, a corporation of Pennsylvania. Patented February 13, 1912.

1,017,023. Manufacture of **Cellulose**. Francis L. Stewart, Murrysville, a., assignor to Maize Sugar and Cellulose Company, Pittsburgh, Pa., a corporation of South Dakota. Patented February 13, 1912.

The method consists in first obtaining a fine bleached pulp from the fiber and cellular matter of maize, and then treating the pulp with chlorinated lime and hydrochloric acid.

1,017,086. Process of Removing Alcohol From and Purifying **Beer**. Henry E. Deckebach, Cincinnati, Ohio. Patented February 13, 1912.

1,017,141. **Paint and Varnish Vehicle**. Carleton Ellis, Larchmont, N. Y. Patented February 13, 1912.

1,017,211. Method of Making **Cement**. William B. Hill, Kansas City, Missouri. Patented February 13, 1912.

1,017,323. **Paint-Vehicle and Furniture Polish**. Joseph Arthur Routhier, Montreal, Quebec, Canada. Patented February 13, 1912.

1,017,360. Process of Enameling **Steel**. David A. York, North Grove, Ind., and Justus A. Tinker, Cleveland, Ohio, assignors of one-third to August W. Kraft, Painesville, Ohio. Patented February 13, 1912.

1,017,473. Method of Producing Practically Pure **Iron**. Arthur P. Scott, Brackenridge, Pa. Patented February 13, 1912.

1,017,593. Process of Making **Amorphous Anhydrous Barium Hydroxid**. Charles Rollin, Newcastle-upon-Tyne, England. Patented February 13, 1912.

1,017,620. Method of Denitrogenizing Practically Pure **Iron**. Robert D. Campbell, Pittsburgh, Pa. Patented February 13, 1912.

1,017,629. Manufacturing and Refining **Copper Alloys**. Walter S. Rockey and Hilliary Eldridge, New York, N. Y., assignors to Metallurgical Research Company, a corporation of Arizona. Patented February 13, 1912.

1,017,636. Process of Preserving **Wood**. Carleton Ellis, Montclair, N. J., assignor to Copper Oil Products Company, a corporation of New York. Patented February 13, 1912.

1,017,669. Solutions of **Perfumes** and Method of Making the Same. Albert Hesse, Wilmersdorf, Germany. Patented February 13, 1912.

1,017,677. Compound and Method of Increasing Combustion of **Coal**, etc. Edward C. Larkin and Joseph F. Duncan, Dayton, Ohio. Patented February 20, 1912.

1,017,807. Method of Producing **Steel Metals**. Auguste J. Rossi, Niagara Falls, N. Y., assignor to The Titanium Alloy Manufacturing Company, New York, N. Y., a corporation of Maine. Patented February 20, 1912.

1,017,912. Manufacture of **Slag Cement**. John Gustaf Adolf Rhodin, London, England. Patented February 20, 1912.

The process comprises causing the chemical combination of finely divided lime with solid finely divided blast furnace slag at a temperature of about 900° C. by means of a suitable contact substance, while improving the hydraulic properties of the resulting slag by simultaneously treating with a finely divided sulfate salt.

1,017,981. Electroplating With **Zinc**. Auguste Arsene Lemetre, Paris, France. Patented February 20, 1912.

1,018,092. Method of Producing **Oxalates**. Launcelot W. Andrews, Davenport, Iowa. Patented February 20, 1912.

1,018,332. **Electroplating Process**. Francis J. McElhone, Jersey City, N. J. Patented February 20, 1912.

1,018,385. **Varnish**. Leo H. Bakeland, Yonkers, N. Y., assignor to General Bakelite Company, New York, N. Y., a corporation of New York. Patented February 20, 1912.

1,018,402. Process of Making **Sulfur Trioxid**. Kurt Albert, Wiesbaden, Germany. Patented February 27, 1912.

1,018,412. **Fluid-Actuated Clutch**. Rudolf Diesel, Munich, Germany. Patented February 27, 1912.

1,018,438. Process for the Precipitation of **Precious Metals** From Cyanid Solutions. James Millar Neil, Toronto, Ontario, Canada, assignor to Alexander M. Hay, Toronto, Canada. Patented February 27, 1912.

1,018,559. Process for Producing **Adhesives**. Richard Heim, Canastota, N. Y., assignor of one-half to Frederick Behrend, New York, N. Y. Patented February 27, 1912.

1,018,733. Process of Manufacturing **Anhydrides of Fatty Acids**. Josef Weber, Essen-on-the-Ruhr, Germany. Patented February 27, 1912.

1,018,734. Process of Treating **Tin-Bearing Material**. Josef Weber, Essen-on-the-Ruhr, Germany, assignor to Th. Goldschmidt, Essen-on-the-Ruhr, Germany, a firm. Patented February 27, 1912.

1,021,768. Process of Treating **Copper Ores**. Rudolph Gahl, Morenci, Ariz. Patented April 2, 1912.

1,021,769. Process of Treating **Ores**. Rudolph Gahl, Morenci, Ariz. Patented April 2, 1912.

1,021,770. **Canning Acid Fruits or Vegetables.** Raymond M. Glacken, Baltimore, Md. Patented April 2, 1912.

This is an improvement in the industry of canning fruits and vegetables in tin, consisting in the reduction of their acidity by subjecting them to ethyl alcohol in the presence of heat and pressure.

1,021,996. **Process of Binding the Active Material of Positive-Pole Lead Electrodes.** William Morrison, Des Moines, Iowa. Patented April 2, 1912.

1,022,085. **Art of Concentration of Mineral Substances.** James M. Hyde, Basin, Mont. Patented April 2, 1912.

1,022,194. **Method of Recovering Resin from Waste Products.** Frank L. Huggins, Wilmington, N. C., assignor of one-half to John P. Moore, Jr., Wilmington, N. C. Patented April 2, 1912.

1,022,274. **Etching Fluid for Flat Printing-Plates of Metal.** Otto Carl Strecker, Eberstadt, near Darmstadt, Germany. Patented April 2, 1912.

1,022,351. **Process of Producing Cyanids and Cyanamids.** Carl Bosch and Alwin Mittasch, Ludwigshafen-on-the Rhine, Germany, assignors to Badische Anilin & Soda Fabrik, Ludwigshafen-on-the-Rhine, Germany. Patented April 2, 1912.

The process consists in the production of sodium cyanid by heating silicon nitrid with carbon in the presence of a sodium salt.

1,022,426. **Arc-Light Electrode or Pencil.** Isador Ladoff, Cleveland, Ohio, assignor of thirty one-hundredths to Philip C. Peck, New York, N. Y. Patented April 9, 1912.

The electrode consists of an iron tube containing a mixture consisting of powdered metallic iron and powdered oxid of titanium.

1,022,466. **Compound for Removing Carbon from Engine-Cylinders.** Daniel E. Cripe, Hillsburg, Ind. Patented April 9, 1912.

1,022,493. **Apparatus for Making Sulfuric Acid.** Curtis C. Meigs, Woodbury, N. J. Patented April 9, 1912.

1,022,551. **Making Radio-Active Beverages.** Herbert Hay Hewitt, London, England. Patented April 9, 1912.

1,022,595. **Process for Producing Alloys of Manganese and Titanium.** Auguste J. Rossi, Niagara Falls, N. Y., assignor to the Titanium Alloy Mfg. Co., New York, N. Y. Patented April 9, 1912.

1,022,600. **Alloys of the Precious Metals and Method of Increasing Hardness of Such Alloys.** Auguste J. Rossi, Niagara Falls, N. Y., assignor to The Titanium Alloy Mfg. Co., New York, N. Y. Patented April 9, 1912.

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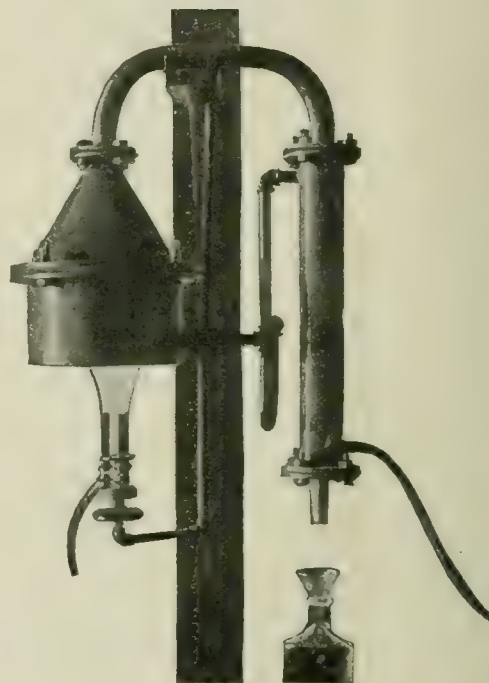
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No. 1.

HEAT TRANSMISSION IN VACUUM EVAPORATOR TUBES.

By HARRY M'CORMACK, H. C. DORMITZER and E. P. ROLESON.

The object of this series of experiments was to determine the efficiencies of a Swenson Evaporator using tubes of four different materials, namely, copper, steel, lead and tin. In order that the results of these tests may be comparable with the work of other investigators, the conditions were carefully recorded. It is known that slight variations in the composition of the metal (impurities) exert considerable influence on the conductivity for heat. In view of this fact, the tubes were carefully sampled and analyzed by standard methods. The auxiliary apparatus, such as scales, gauges, thermometers, etc., was tested for accuracy and the necessary corrections made. The steam gauge was tested on a Crosby Steam Gauge Tester and the vacuum gauge was calibrated against a mercury column. The scales used for weighing the water necessary were compared with a standard balance. The thermometers were checked up against a thermometer standardized by the U. S. Government Bureau of Standards.

APPARATUS.

The evaporator used was of the single effect Swenson type, especially designed for experimental purposes. The dimensions and details are clearly shown by Fig. 1. The general arrangement of piping and auxiliary apparatus is shown by Figs. 2 and 3. The walls of the evaporator are of $\frac{1}{2}$ in. cast iron bolted with three-eighths bolts. The steam enters the steam chest by means of a $\frac{1}{4}$ in. pipe, passes through the heating tube into the exhaust chamber and flows out through a 1 in. drain in to the weighing tank. Thirty-two steam tubes were used in each test. The tubes are fitted into holes bored in the plate separating the steam chest from the body of the evaporator proper, and made steam tight by rubber gaskets. The whole is held firmly in place by cast iron plates bolted to the frame.

The vapors are led to the condenser by a 5 in. cast iron pipe, condensed by a spray of cold water and drawn off by a steam pump. The pump is made by the American Steam Valve & Pump Co. and has dimensions as follows:

Steam cylinder diameter.....	4	inches
Water cylinder diameter.....	3	inches
Piston rod diameter.....	$\frac{7}{8}$	inch
Stroke.....	6	inches

The cooling water and condensed steam were collected in weighing tanks and the amount recorded.

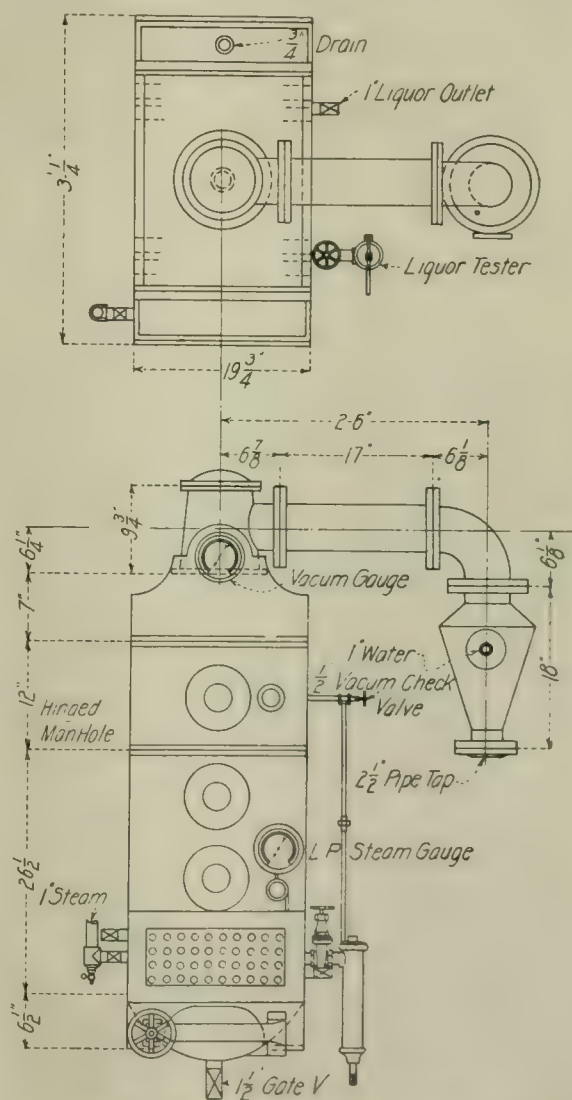


Fig. 1—Arrangement of Evaporator.

METHOD.

The cold evaporator was filled with water to a depth of 2 ins. above the tubes and a preliminary run made to heat up the apparatus. The time necessary for this run averaged 20 minutes. When one run was started immediately after the close of the one preceding, this

preliminary heating was unnecessary. When the evaporator was thoroughly heated the water was taken out and a weighed amount of hot water put in; 180 lbs. was found to fill the evaporator to the desired level. At a definite time, the temperature of the water was taken and the evaporator closed for the run. The exhaust valve was opened a measured amount and the steam valve opened sufficiently to give the desired pressure, ranging between 5 and 10 lbs. gauge pressure. The pump is started and the cooling water turned on. Readings of steam pressure, vacuum and the temperature of the exhaust steam were taken every five minutes. Each run lasted two hours. In order to keep the water level in the evaporator constant, water in measured amounts at definite temperatures was added as needed. In order to keep the condensed steam from evaporating cold water in measured amounts was added to the container. At the end of the run the pump, cooling water and live steam were turned off and the steam tubes allowed to drain. The water remaining in the evaporator was weighed and its temperature taken. This cycle of operations was repeated for each run.

The vacuum gauge was calibrated by comparison with mercury column, the readings being as follows:

No.	Mercury column. Inches.	Gauge readings before adjustment.	
		Inches.	Up.
1	19.0	19.3	
2	18.0	18.4	
3	17.0	17.2	
4	16.0	16.5	
5	15.0	15.4	
6	14.25	14.8	
7	13.25	13.8	
8	12.25	12.8	
9	11.0	11.4	
10	10.0	10.5	
11	7.0	7.8	

No attempt was made to correct the gauge. The readings were corrected by means of the curve plotted from the data. Fig. 4 shows the curve.

The pressure gauge was calibrated by comparison with square inch tester. The gauge readings in pounds being as follows:

No.	Reading gauge tester, lbs.	Gauge reading in lbs. before adjustment.		
		Up.	Down.	Mean.
1	5	3.8	3.7	3.75
2	7	5.6	5.6	5.6
3	9	7.6	7.6	7.6
4	11	9.7	9.6	9.65
5	13	11.6	11.5	11.55
6	15	13.4	13.5	13.45
7	17	15.4	15.5	15.45
8	19	17.3	17.3	17.3
9	21	19.3	19.3	19.3
10	23	21.2	21.2	21.2
11	25	23.0	23.1	23.05
12	27	25.0	25.0	25.0
13	29	26.9	26.8	26.85
14	31	28.9	28.9	28.9

No attempt was made to correct the gauge. The readings being corrected by means of the curve plotted from these data. The curve is shown in Fig. 5.

METHODS OF ANALYSIS.

In making the analyses of the four sets of tubes used in this set of tests, the best available methods were used. It was necessary to determine carbon,

sulphur, phosphorus and manganese in the steel; to determine copper, copper oxide, lead, tin, and zinc in the copper tubes; to determine tin, lead antimony and zinc in the tin tubes and to determine lead, antimony, tin and zinc in the lead tubes. In order to save space

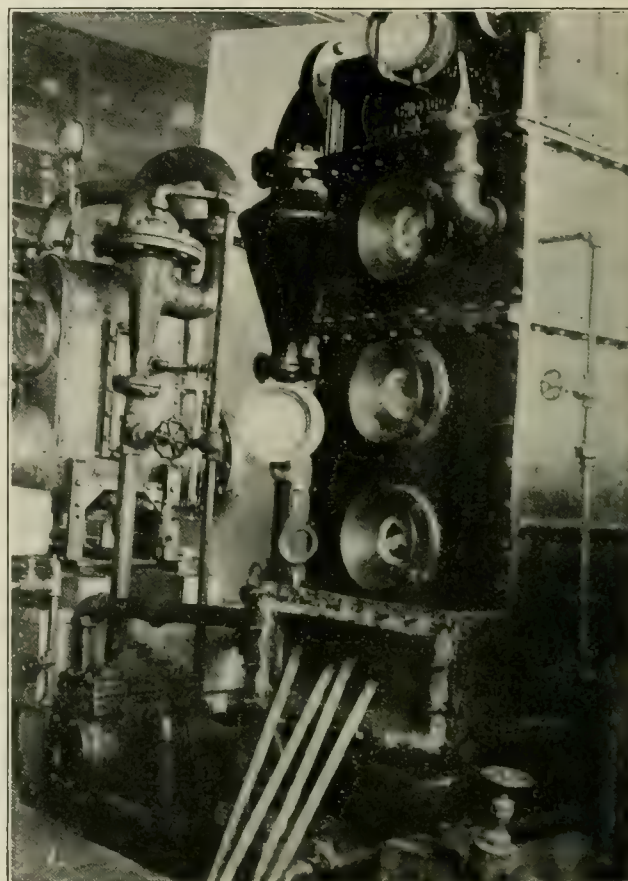


Fig. 2—Arrangement of Piping and Auxiliary Apparatus.

the analyses of the last three tubes will be described as though they were alloyed and an analysis of this alloy had to be made.

Carbon is determined by the color method; 0.5 gm. duplicates of the sample and the standard are weighed into test tubes of about 30 cc. capacity; 15 cc. of nitric acid (sp. gr. 1.2) is added to each test tube. The tubes are put in a metal beaker of about 600 cc. capacity and boiled for ten minutes. At the end of this time everything should be in solution. If, on account of the large size of the samples, they will not dissolve in this time, boil them longer. The sample and standard should be boiled an equal length of time. The two are compared in the regular colorimetric tubes and the per cent carbon in the sample figured directly.

Sulphur is determined by the evolution method; 5 gms. of the sample and an equal amount of the standard are weighed into 500 cc. Erlenmeyer flasks; 150 cc. of HCl (1-1) is added through a thistle tube, which projects below the level of the acid in the Erlenmeyer. The hydrogen generated, carrying with it the H_2S formed from the sulphur compounds of the steel, passes through a glass tube into an absorption flask, in which has been placed 30 cc. of a 10 per cent solution

of cadmium chloride, containing at least 20 per cent of ammonium hydroxide. The flask is gently heated until all the steel is in solution. The contents are then brought to a boil and the connection between the flask and the absorption bulb broken as soon as the condensed steam commences to drip into the bulb. The contents of the absorption flask are made acid with HCl after the addition of a slight excess of N/20 iodine solution. The blue color, which appears on the addition of starch solution, is discharged with N/20 sodium thio-sulphate. The per cent of sulphur in the sample is determined by direct comparison with the standard which is run at the same time.

Phosphorus is titrated with sodium hydroxide solution; 5.0 gms. of the steel is weighed into a 500 cc. Erlenmeyer flask, and is dissolved in nitric acid (1-2) by gentle heating. When solution is complete, enough of a saturated solution of potassium permanganate is added to give a permanent heavy brown precipitate. The solution is boiled to ensure complete oxidation, cooled slightly and the manganese dioxide dissolved by adding a pinch of sugar. The solution is cooled to room temperature and enough ammonium hydroxide added to make the solution an amber color. This should bring the temperature to about 60° C.; 50 cc. of an ammoniacal solution of molybdic acid is added and the flask shaken well. The precipitated phosphomolybdate is filtered off, washed free from nitric acid and titrated with standard sodium hydroxide.

Manganese is determined by Ford's method; 5.0 grams of the steel is weighed into a 500 cc. beaker and dissolved in nitric acid (1-1); 100 cc. of nitric acid (sp. gr. 1.42) and 10 grams of potassium chlorate are added and the solution boiled until the precipitation of manganese dioxide is complete. The manganese dioxide is filtered out on asbestos, using a suction pump, dissolved in a definite amount of standard ferrous sulphate solution and the excess of ferrous sulphate solution titrated with potassium permanganate.

ALLOY.

Antimony and *tin* are weighed together as the oxides, and the amount of antimony determined on a separate sample. The alloy is dissolved in nitric acid (sp. gr. 1.2) and evaporated to moist dryness. The beaker is allowed to cool and cold distilled water added in large quantities, at least 75 cc. The oxides are filtered out, the filter paper dried and placed in a crucible. The crucible is heated slowly until all the carbon is consumed, and then at a dull red heat to constant weight.

Antimony is titrated in a separate sample with KMnO_4 solution. It is necessary to standardize the permanganate solution against antimony, as the theoretical antimony value does not agree with that actually obtained. The variation is slight but is sufficient to cause some error. Weight of antimony in sample in proportion to tin must be known approximately, and this proportion maintained in the standardization. Weigh 0.1202 grams powdered CP anti-

mony into a 500 cc. Erlenmeyer. Add the proper amount of CP tin. Add 3 gm. K_2SO_4 and 10 cc. H_2SO_4 (1.84). Heat to solution over a small naked flame. Cool, add 50 cc. distilled water and 2 grams tartaric acid. Heat to boiling and boil for 5 minutes. Cool, add 110 cc. water and 25 cc. HCl (1.2 sp. gr.). Titrate with KMnO_4 to first permanence of pink color throughout the solution.

Lead is determined in the filtrate from the combined oxides; 10 cc. of conc. sulphuric acid is added after filtering out the oxides and the solution evaporated to dryness or to copious fumes of sulphuric anhydride. The lead sulphate is filtered out on a gooch crucible, washed with a dilute sulphuric acid solution and alcohol, dried and weighed. The residue is made alkaline with ammonia and any *copper* noted by the presence of a blue color. *Iron* and *aluminum* if present will precipitate at this point and may be filtered out and weighed in the usual manner. If any *copper* is present it will be determined as the sub-iodide. The ammoniacal solution is acidified with acetic acid, and sulphurous acid added to excess. Fifty cc. of 10 per cent potassium iodide solution is added and the solution boiled until the precipitate becomes granular. It is then filtered on a gooch crucible and weighed as CuI ; the per cent of copper being calculated directly.

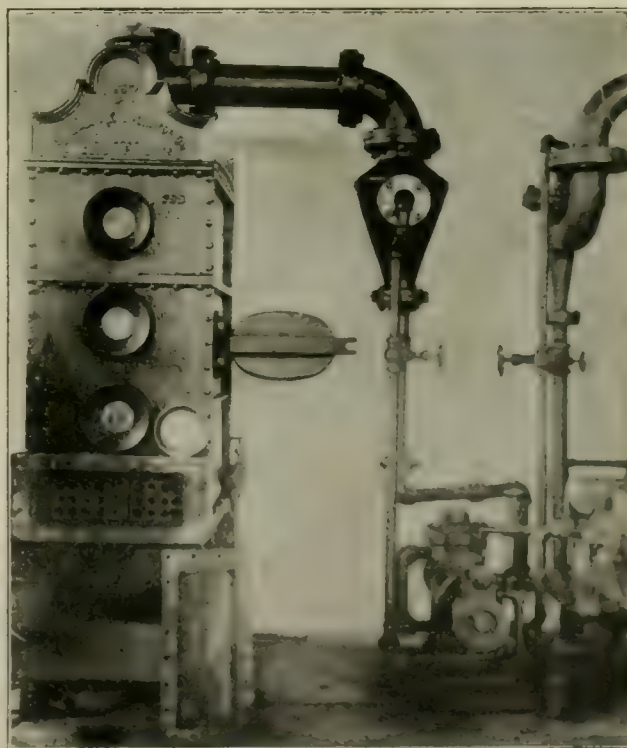


Fig. 3—Arrangement of Piping and Auxiliary Apparatus.

Zinc is determined in the filtrate from the copper. The solution is made ammoniacal, after boiling out the sulphurous acid. It is quite frequently necessary to filter at this point owing to the precipitation of sulphur. The solution is made barely acid with hydrochloric acid, and 50 cc. of sodium ammonium phosphate added. The zinc is precipitated as zinc am-

monium phosphate, $\text{Zn}_2\text{P}_2\text{O}_7$. The precipitate is granulated by boiling, filtered out, and ignited in a porcelain crucible.

Table I contains data on the tube and Tables II to IX show the runs.

TABLE I.—DATA ON TUBES.

Steel—		mm.
Carbon, 0.10 per cent	Average outside diameter....	19.02
Manganese, 0.39 per cent	Average inside diameter....	16.56
Sulphur, 0.02 per cent		2.46
Phosphorus, 0.016 per cent	Average thickness.....	1.23
Copper—		
Copper, 99.92 per cent	Average outside diameter....	19.00
No impurities	Average inside diameter....	16.41
	Average thickness.....	2.59
	Average thickness.....	1.29
Lead—		
Antimony, 9.6 per cent	Average outside diameter....	19.98
Lead, 90.2 per cent	Average inside diameter....	12.61
No other metals		7.37
	Average thickness.....	3.68
Tin—		
Antimony, 0.4 per cent	Average outside diameter....	19.01
Tin, 99.6 per cent	Average inside diameter....	12.61
		6.40
	Average thickness.....	3.20

The actual length of the tubes is 25 ins.

The effectual length (in contact with water) is 24 ins.

TABLE II.—COPPER TUBES—FIRST RUN.

Time—Hours.	Steam pressure, Pounds—Gauge.	Vacuum, Inches Hg.	Temperature Exhaust Steam.
0:00	10.0	20.0	80° C.
5	10.2	20.8	80.0
10	9.5	23.0	79.0
15	10.9	23.3	75.0
20	10.2	23.8	72.0
25	10.0	24.0	71.0
30	9.8	24.1	69.5
35	10.2	24.1	70.0
40	10.5	23.9	70.0
45	7.0	24.0	76.0
50	10.2	23.5	76.0
55	7.2	23.9	76.5
1:00	7.9	23.8	78.5
5	8.5	23.5	79.0
10	9.0	23.9	78.0
15	10.2	23.9	75.0
20	11.5	23.8	76.0
25	12.3	23.7	76.0
30	11.8	23.8	75.0
35	11.5	24.0	77.0
40	11.1	24.0	76.0
45	9.8	24.2	72.0
50	10.8	24.1	75.0
55	12.5	24.1	77.0
2:00	16.1	24.1	76.0

Water added #.	Water removed #.	Condensed steam #.	Cold water added to condense steam #.
180 at 50° C.	92.5 #	24.5	30.0
26 57.5		29.0	30.0
25 51		26.0	30.0
26.7 60		24.5	30.0
27 62		26.0	
28.5 50		26.7	
22.5 51		27.0	
		25.0	
		27.5	
		24.0	
		22.5	
		20.5	
		23.0	
		24.0	
		24.5	
		25.5	
		26.5	

Average steam pressure, lbs.—

Gauge	10.3
Corrected	11.8
Absolute	26.5
Quality of steam, per cent.....	95.0
Latent heat of vaporization at 26.5 lbs., B. T. U.....	949.2
Temperature of steam at 26.5 lbs., degs. F.....	243.7
Average temperature of exhaust steam, degs. F.....	75.4 C 167.7
Gross weight condensed steam, lbs.....	426.7
Water added to condense steam, lbs.....	120.0
Net weight condensed steam, lbs.....	306.7
Heat given up by steam cooling 243.7°—167.7° (76° F.):	
306.7×76.....	23,300
Heat given up by steam condensing:	
306.7×95%×949.2	276,600
Heat used (B. T. U.)	299,900

Average vacuum in evaporator—

Gauge, Hg.....	23.6
Corrected	23.2
Pounds absolute.....	3.3
Latent heat of vaporization at 3.3 lbs., B. T. U.....	1,010.0
Temperature at boiling point, 3.3 lbs. pressure, degs. F.	145.3
Heat used to raise water added to boiling point:	
Lbs. B. T. U.	
180 at 50 C.—122 F., 180×23.3.....	4,200
26 at 57.5—135.5, 26×9.8.....	250
25 at 51—123.8, 25×21.5.....	540
26.7 at 60—140.0, 26.7×5.3.....	140
27 at 62—143.6, 27×1.7.....	50
28.5 at 50—122, 28.5×23.3.....	670
22.5 at 51—123.8, 22.5×21.5.....	490

B. T. U. 6,340

Total water added, lbs.....	335.7
Water removed.....	92.5
Water evaporated.....	243.2

Heat used to vaporize 243.2 lbs. of water, $243.2 \times 1,010 =$

245,600 B. T. U.

Total heat used, 251,940 B. T. U.

Efficiency, 83.8 per cent.

TABLE III.—COPPER TUBES—SECOND RUN.

Time—Hours.	Steam pressure, Pounds—Gauge.	Vacuum, Inches Hg.	Temperature Exhaust Steam.
0:00	5.5	24.0	174° F.
5	5.3	23.6	173
10	7.0	24.6	169
15	7.4	24.5	170
20	7.9	24.5	170.5
25	8.6	24.3	170
30	7.8	24.0	167
35	7.3	24.1	165.5
40	6.2	24.1	165
45	7.5	24.2	165
50	6.5	22.8	168
55	6.0	23.7	168
1:00	8.1	24.1	168
5	6.2	23.3	178
10	5.7	23.0	172
15	3.8	24.2	163
20	7.2	24.3	168
25	11.0	24.1	182
30	10.4	23.6	185
35	9.0	24.0	185
40	12.5	20.6	195
45	7.5	22.1	181
50	9.7	23.9	179
55	13.4	23.3	185
2:00	15.0	23.0	186

Water added, # at ° F.	Water removed.	Condensed steam #.	Cold water added to condense steam.
180 at 142 F.	129.5 #	28.5	30 #
25.5 at 138.5		25.5	30
27.5 at 142		27.7	30
24.2 at 139		25.5	
25 at 133		24.2	
25 at 138.5		25.0	
26 at 148		25.0	
24 at 153		26.5	
25.5 at 151		27.5	
23 at 143		25.0	
		24.0	
		25.5	
		23.0	
		22.5	
		24.0	
		24.5	
		25.5	
		29.5	

Average steam pressure, lbs.—	
Gauge	8.1
Corrected	9.4
Absolute	24.1
Quality of steam, per cent.	95.0
Latent heat of vaporization at 24.1 lbs., B. T. U.	952.7
Temperature of steam at boiling, 24.1 lbs., degs. F.	238.0
Average temperature of exhaust steam.	174.1
Gross weight condensed steam.	433.4
Water added to condense steam.	90.0
Net weight condensed steam.	343.4
Heat given up by steam in cooling from 238.0 to 174.1, or 63.9° F.:	

	B. T. U.
343.4×63.9	21,940
Heat given up by steam condensing:	
0.95×343.4×952.7	310,700

Total	332,640
Average vacuum in evaporator—	
Gauge, Hg.	23.7
Corrected, Hg.	23.2
Pounds absolute.	3.3
Latent heat of vaporization at 3.3 lbs., B. T. U.	1,010.0
Boiling temperature at 3.3 lbs., degs. F.	145.3
Total water added, lbs.	405.7
Water removed.	129.5
Water evaporated.	276.2

Heat to raise added water to boiling temperature:	
180# at 142° F.	180 × 3.3 = 595
25.5 at 138.5	25.5 × 6.8 = 173
27.5 at 142	27.5 × 3.3 = 91
24.2 at 139	24.2 × 6.3 = 152
25 at 138.5	25 × 6.8 = 170
25 at 133	25 × 12.3 = 310
26 at 148	26 × 2.7 = 70
24 at 153	24 × 7.7 = 185
25.5 at 151	25.5 × 5.7 = 145
23 at 143	23 × 2.3 = 53
	1,554
	400

Heat to vaporize 276.2 lbs., 279,000.
Total, 280,150.
Efficiency, 85.2 per cent.

TABLE IV.—COPPER TUBES—THIRD RUN.

Time—Hours, Minutes.	Steam pressure, Pounds—Gauge.	Vacuum, Inches Hg.	Temperature Exhaust Steam.
5	11.0	23.5	169
10	8.5	25.0	156
15	9.0	25.1	156
20	8.5	25.0	156
25	7.8	25.0	159
30	6.9	24.5	155
35	7.3	24.5	163
40	6.2	24.5	164
45	8.5	24.2	166
50	9.5	24.2	170
55	8.5	24.5	167
1:00	12.0	24.2	174
5	10.1	24.9	170
10	6.0	25.1	165
15	10.6	25.0	174
20	8.6	24.5	170
25	8.5	25.0	167
30	9.5	25.0	168
35	10.1	25.1	168
40	10.8	25.1	168
45	10.8	24.8	169
50	11.1	24.9	167
55	11.3	24.9	167
2:00	11.8	24.7	169

Water added, at ° F.		Cold water added to condense steam.	
180# at 144°	169 #	27.5 #	30 #
27.5 at 122		25.0	30
25 at 129		25.0	30
24 at 130		26.5	
25 at 131		24.0	
25.5 at 138		23.5	
23.5 at 129		25.0	
28 at 146		25.0	
		25.5	
		28.0	
		29.0	
		28.5	
		14.0	

Average steam pressure, lbs.—	
Gauge	9.3
Corrected	10.7
Absolute	25.4
Quality of steam, per cent.	95.0
Latent heat of vaporization at 25.4 lbs., B. T. U.	950.8
Boiling temperature at 25.4 lbs., degs. F.	240.9
Average temperature of exhaust steam, lbs.	165.9
Gross weight condensed steam, lbs.	326.5
Water added to condense steam, lbs.	90.0
Net weight of condensed steam, lbs.	236.5
Heat given up by steam cooling from 240.9 to 165.9, or 75° F.:	

	B. T. U.
236.5×75	17,700
Heat given up by steam in condensing:	
236.5×0.95×950.8	213,600

Total B. T. U. given to evaporator.	231,300
Water evaporated, lbs.	189.5
Average vacuum in evaporator, lbs. Hg.—	
Gauge	24.7
Corrected	24.3
Pounds absolute.	2.8
Latent heat of vaporization at 2.8 lbs., B. T. U.	1,014.1
Boiling temperature at this pressure, 2.8 lbs., degs. F. ...	138.4
Heat used to raise water added to boiling point:	

180 lbs. at 144° F.	180×5.6 = 1,010
27.5 at 122	27.5×16.4 = 450
25 at 129	25 × 9.4 = 236
24 at 130	24 × 8.4 = 200
25 at 131	25 × 7.4 = 184
23.5 at 129	23.5 × 9.4 = 220
25.5 at 138	25.5 × 0.4 = 10
28 at 146	28×7.6 = 210
	1,300
	1,220

Heat to vaporize 189.5 lbs. of water, 189.5×1,014.1=192,200
B. T. U.
Total B. T. U., 192,280.
Efficiency, 82.9 per cent.

TABLE V.—TIN TUBES—FIRST RUN.

Time—Hours, Minutes.	Steam pressure, Pounds—Gauge.	Vacuum, Inches Hg.	Temperature Exhaust Steam.
0:00	11.0	19.5	178
5	9.8	24.3	180
10	10.8	25.0	182
15	9.5	25.0	176
20	9.0	25.0	175
25	10.0	24.1	174
30	9.8	24.9	178
35	9.7	25.1	181
40	10.2	25.1	183
45	11.2	25.1	181
50	10.6	25.2	180
55	10.0	25.2	177
1:00	9.6	25.2	179
5	9.5	24.9	178
10	9.1	25.2	178
15	9.9	24.6	175
20	9.8	25.2	183
25	10.0	25.3	186
30	10.1	25.2	181
35	10.1	25.3	177
40	10.1	25.2	174
45	10.1	25.2	172
50	9.5	25.2	172
55	5.8	25.3	174
2:00	7.8	24.8	173

Water added at ° F.		Cold water added to condense steam.	
180 # at 125.5	128	27	30
23.7 at 130		23.7	30
24.5 at 135		24.5	30
28.7 at 126.5		28.5	
29.5 at 123		28.7	
24.5 at 125.5		29.5	
		24.5	
		25.0	
		24.2	
		25.5	
		25.5	
		27.5	
		29.7	

Average steam pressure, lbs.—

Gauge	9.7
Corrected	11.1
Absolute	25.8
Quality of steam, per cent.	95.0
Latent heat of vaporization at 25.8 lbs., B. T. U.	950.2
Boiling temperature of steam at this pressure, deg. F.	241.7
Average temperature of exhaust steam, deg. F.	177.9
Gross weight condensed steam, lbs.	343.8
Water added to condense steam, lbs.	90.0
Net weight steam used, lbs.	253.8

Heat given up by steam in cooling from 241.7 to 177.9, or 63.8° F.:

B.T.U.	
253.8×63.8	16,200

Heat given up by steam in condensing:	
253.8×0.95×950.2	229,200

Total 245,400

Average vacuum in evaporator, lbs. Hg.—

Gauge	25.2
Corrected	24.8
Pounds absolute	2.5
Latent heat of vaporization at 2.5 lbs., B. T. U.	1,017.0
Temperature of steam at this pressure, 2.5 lbs., deg. F.	133.8
Total water added, lbs.	310.9
Water removed, lbs.	128.0
Water evaporated, lbs.	182.9

Heat to raise added water to boiling temperature:

180 # at 125.5	180 × 8.3=1,490	
23.7 at 130	23.7 × 3.8= 90	
24.5 at 135		24.5×1.2=30
28.7 at 126.5	28.7 × 7.3= 210	
29.5 at 123	29.5×10.8= 320	
24.5 at 125.5	24.5 × 8.3= 200	

2,310

30

Heat to vaporize water, 182.9×1,017=186,950.

Total B. T. U., 189,230.

Efficiency, 77.1 per cent.

TABLE VI.—TIN TUBES—SECOND RUN.

Time—Hours, Minutes.	Steam pressure, Pounds—Gauge.	Vacuum, Inches Hg.	Temperature Exhaust Steam.
0:00	1.0	21.2	184
5	5.1	22.5	180
10	5.5	21.2	188
15	6.4	21.0	187
20	6.3	21.0	190
25	6.5	21.4	188
30	6.9	21.7	187
35	6.9	21.8	187
40	5.9	21.8	182
45	5.5	21.2	182
50	4.7	21.8	184
55	6.5	23.0	184
1:00	6.0	22.0	186
5	6.3	22.0	190
10	7.5	22.3	183
15	6.5	22.5	179
20	6.5	22.5	178
25	6.2	22.5	183
30	5.2	21.9	182
35	5.0	22.6	183
40	6.5	22.8	183
45	6.1	23.0	179
50	6.2	23.0	177
55	6.2	23.0	175
2:00	5.9	22.1	185

Water added at ° F.	Removed water.	Condensed steam.	Water to condense steam.
180 # at 143 F.	122#	27.8#	30#
24.5		24.5	30
25.0		25.0	30
25		26.5	
27		25.0	
24		27.0	
24.5		22.0	
		23.5	
		27.0	
		24.0	
		22.0	
		24.7	
		28.5	
		27.0	
		27.0	

Average steam pressure, lbs.—

Gauge	5.9
Corrected	7.2
Absolute	21.9
Quality of steam, per cent.	95.0
Latent heat of vaporization at 21.9 lbs., B. T. U.	956.2
Boiling temperature at 21.9 lbs., deg. F.	232.7
Average temperature of exhaust steam, deg. F.	183.6
Gross weight condensed steam, lbs.	381.5
Water added, lbs.	90.0
Net weight steam used, lbs.	291.5

Heat given up by steam in cooling from 232.7 to 183.6, or 49.1° F.:

B.T.U.	
291.5×49.1	14,300

Heat given up by steam in condensing:	
291.5×956.2×0.95	264,800

Total 279,100

Average vacuum in evaporator, ins. hg.—

Gauge	22.1
Corrected	21.7
Pounds absolute	4.1
Latent heat of vaporization at 4.1 lbs., B. T. U.	1,005.0
Temperature of steam at 4.1 lbs., deg. F.	153.9

Heat to raise added water to the boiling point:

180 # at 143 F.	180 × 10.9=1,980
24.5 at 146	24.5 × 7.9= 190
25 at 144	25 × 9.9= 240
25 at 146	25 × 7.9= 190
27 at 138	27 × 15.9= 430
24 at 137	24 × 16.9= 410
24.5 at 143	24.5 × 10.9= 270
	3,710

Water added, lbs. 330.0

Water removed, lbs. 122.0

Water evaporated, lbs. 208.0

Heat to evaporate water, 208×1,005=209,000 B. T. U.

Total, 212,700 B. T. U.

Efficiency, 76.2 per cent.

TABLE VII.—STEEL TUBES—FIRST RUN.

Time—Hours, Minutes.	Steam pressure, Pounds—Gauge.	Vacuum, Inches Hg.	Temperature Exhaust Steam.
0:00	4.6	21.3	164
5	4.8	22.1	168
10	6.1	23.2	171
15	7.0	23.0	167
20	6.5	22.8	169
25	6.6	21.9	171
30	6.8	22.1	173
35	7.6	22.1	176
40	7.9	22.2	170
45	8.0	22.4	168
50	7.8	22.1	165
55	7.4	21.8	166
1:00	7.2	22.0	169
5	7.5	22.1	170
10	9.0	22.1	170
15	8.3	22.4	172
20	7.1	22.3	173
25	6.7	22.4	169
30	6.8	22.1	173
35	7.2	22.6	171
40	7.3	22.5	170
45	7.1	22.7	169
50	6.9	22.7	170
55	7.3	22.7	170
2:00	7.1	22.3	169

Water added #.	Water removed #	Condensed steam, gross #.	Cold water added to condense steam #.
180 at 140° F.			
26.5 at 130	107	26.5	30
22.5 at 138		22.5	30
28 at 142		25.6	30
27 at 137		28	30
21.5 at 135		27	
26.7 at 139		21.5	
28 at 140		26	
29.2 at 141		26.7	
22 at 135		29.5	
		27.7	
		28	
		23.8	
		29.2	
		26.5	
		22	

Quality of steam, per cent.	95.0
Average steam pressure, lbs.—	
Gauge	7.1
Corrected	8.4
Absolute	23.1
Average temperature exhaust steam, degs. F.	169.8
Latent heat of vaporization at 23.1 lbs., B. T. U.	954.4
Temperature of steam at 23.1 lbs., degs. F.	235.7
Gross weight of condensed steam, lbs.	390.3
Net water added, lbs.	120.0
Net weight steam used, lbs.	270.3
Heat given up by steam in cooling from 235.7 F. to 169.8, or 65.9 F.:	

270.5×65.9	B.T.U.
Heat given up by steam in condensing:	17,800
270.5×0.95×954.4	245,100

Total heat	262,900
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Average vacuum in evaporator—	
Gauge, ins. Hg.	22.3
Corrected, ins. Hg.	22.0
Pounds absolute	3.9

Temperature at 3.9 lbs., degs. F.	151.9
Latent heat of vaporization at 3.9 lbs., B. T. U.	1,006.2
Water added, lbs.	311.4
Water removed, lbs.	107.0
Water evaporated, lbs.	204.4

Heat to raise added water to boiling point:	
180# at 140	180 × 11.9 = 2,160
26.5 at 130	26.5 × 22.9 = 600
22.5 at 138	22.5 × 13.9 = 310
28 at 142	28 × 9.9 = 280
27 at 137	27 × 14.9 = 400
21.5 at 135	21.5 × 16.9 = 360
26.7 at 139	26.7 × 12.9 = 340
28 at 140	28 × 11.9 = 340
29.2 at 141	29.2 × 10.9 = 320
22 at 135	22 × 16.9 = 370

5,480 B. T. U.

Heat to vaporize water, 204.4×1,006.2=205,500.

Total, 210,980 B. T. U.

Efficiency, 80.2 per cent.

TABLE VII.—STEEL TUBES—SECOND RUN.

Time—Hours, Minutes.	Steam pressure, Pounds—Gauge.	Vacuum, Inches Hg.	Temperature Exhaust Steam.
0:00	4.2	23.2	172° F.
5	6.8	23.0	174
10	6.5	23.2	176
15	7.2	23.2	175
20	6.8	22.8	170
25	7.1	22.9	176
30	7.0	23.0	174
35	8.0	23.3	168
40	6.9	23.2	170
45	8.2	23.3	178
50	7.5	22.9	177
55	7.3	23.1	171
1:00	7.6	23.2	173
5	5.2	22.2	169
10	6.6	23.3	166
15	7.2	23.3	173
20	6.8	23.2	172
25	7.6	23.3	170
30	7.3	23.3	172
35	6.5	23.1	170
40	6.6	23.2	171
45	6.9	23.3	174
50	7.6	23.2	170
55	7.0	23.2	172
2:00	6.9	23.1	172
Water added, lbs. at 143° F.	Water removed, 115.2#	Condensed steam—gross, 25.5#	Water for con- densing steam, 30#
180# at 143° F.		24.5	30
24.5 at 150		28.2	30
26 at 146		23.7	30
27.5 at 148		23	
28.2 at 135		26	
26 at 140		27	
27 at 141		24.7	
		25	
		26.5	
		27.2	
		25.5	
		29	
		28.2	
		25	

Average steam pressure, lbs.—	
Gauge	6.9
Corrected	8.3
Absolute	23.0
Quality of steam, per cent.	95.0
Average temperature of exhaust steam, degs. F.	172.0
Latent heat of vaporization at 23 lbs., B. T. U.	954.4
Temperature of steam at 23 lbs., degs. F.	235.5
Weight of condensed steam—gross, lbs.	418.0
Water added, lbs.	120.0
Steam used, lbs.	298.0
Heat given up by steam cooling from 235.5 to 172 F., or 63.5 F.:	

298×63.5	B.T.U.
Heat given up by steam condensing:	18,900
298×0.95×954.4	270,100

Total B. T. U.	289,000
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Average vacuum in evaporator—	
Gauge, ins. Hg.	23.1
Corrected, ins. Hg.	22.8
Pounds absolute	3.5

Latent heat of vaporization at 3.5 lbs., B. T. U.	1,008.3
Temperature of steam at 3.5 lbs., degs. F.	147.2
Water added, lbs.	339.2
Water removed, lbs.	115.2
Water evaporated, lbs.	224.0

Heat to raise added water to boiling point:	
180# at 143, 180×4.2	750
24.5 at 150,	
26 at 146, 26×1.2	30
27.5 at 148,	
28.2 at 135, 28.2×12.2	340
26 at 140, 26×7.2	190
27 at 141, 27×6.2	170

1,480

Heat to vaporize water, 224×1,008.3=225,600.

Total 227,000 B. T. U.

Efficiency, 78.7 per cent.

TABLE VIII.—LEAD TUBES—FIRST RUN.

Time—Hours, Minutes.	Steam pressure, Pounds—Gauge.	Vacuum, Inches Hg.	Temperature Exhaust Steam.
5	7.2	22.2	160
10	8.5	23.5	150
15	8.5	24.0	149
20	8.0	23.9	147
25	3.8	24.9	148
30	5.1	23.0	149
35	4.9	22.1	149
40	4.6	23.0	148
45	4.6	23.1	147
50	4.9	23.0	147
55	5.2	22.6	149
1:00	7.5	23.1	147
5	8.5	23.5	148
10	8.1	23.2	148
15	9.0	23.5	149
20	9.0	23.2	149
25	9.1	23.1	150
30	9.0	23.5	148
35	8.8	23.2	149
40	9.0	23.5	149
45	9.0	22.8	149
50	9.0	23.5	148
55	10.5	23.5	149
2:00	10.5	27.5	149
Water added, lbs. at degs. F.	Water removed, lbs.	Condensed steam, gross, lbs.	Cold water added, lbs.
180 at 135° F.	137	24.0	30
24 at 127		24.0	30
23.7 at 127		25.8	
27 at 129		26.1	
28 at 131		23.7	
21.5 at 131		27.0	
28 at 138		26.0	
27 at 131		28.0	
27 at 130		21.5	
27.5 at 129		28.0	
27 at 135		27.0	
		24.0	
		27.0	
		27.5	
		27.0	
		23.5	
		24.0	
		22.8	
		0.1	

Average steam pressure, lbs.—

Gauge	7.3
Corrected	8.7
Absolute	23.4
Latent heat of vaporization at 23.4, B. T. U.	953.3
Temperature of steam at this pressure, degs. F.	236.0
Quality of steam, per cent.	95.0
Total condensed steam, lbs.	465.0
Water added	60.0
Condensed steam, net.	405.0
Average temperature exhaust steam, degs. F.	149.0
Heat given up by steam in cooling from 236 to 149 or 87° F.:	B. T. U.
405×87	35,200
Heat given up by steam in condensing:	
405×0.95×953.3	366,700

Total 401,900

Average vacuum in evaporator—

Gauge, ins. hg.	23.3
Corrected, ins. hg.	23.0
Absolute, lbs. abs.	3.5
Latent heat of vaporization at 3.5 lbs., B. T. U.	1,009.0
Temperature of steam at 3.5 lbs., degs. F.	147.7
Total water added, lbs.	440.7
Total water removed	137.0
Water evaporated	303.7
Heat to raise added water to boiling point:	B. T. U.
180# at 135° F., 180×12.7	2,285
24 at 127, 24×20.7	497
23.7 at 127, 23.7×20.7	492
27 at 129, 28×18.7	524
28 at 131, 21.5×16.7	360
21.5 at 131, 27×16.7	451
28 at 138, 28×9.7	272
27 at 131, 27×17.7	478
27 at 130, 27×18.7	505
27.5 at 129, 27.5×18.7	515
27 at 135, 27×12.7	343

Heat to vaporize water: 6,720
 303.7×1,009 306,400

Total 313,100

Efficiency, 78.1 per cent.

TABLE IX.—LEAD TUBES.

Time—Hours, Minutes.	Steam pressure, Pounds—Gauge.	Vacuum, Inches Hg.	Temperature Exhaust Steam.
5	8.2	23.3	157
10	7.3	21.8	151
15	7.5	24.0	147
20	7.2	24.5	148
25	7.5	24.0	151
30	7.3	23.3	147
35	7.0	24.1	148
40	7.0	24.0	148
45	7.0	23.5	151
50	7.3	23.3	149
55	7.1	23.9	148
1:00	7.9	23.2	148
5	6.1	23.3	150
10	6.4	23.7	149
15	7.0	23.2	151
20	7.3	22.0	152
25	7.4	22.9	152
30	8.0	22.8	151
35	7.3	23.0	151
40	7.3	22.8	152
45	7.3	23.0	156
50	9.0	23.6	153
55	9.7	23.0	148
2:00	3.0	23.3	146

Water added, lbs. at degs. F.	Water removed, lbs.	Condensed steam, gross lbs.	water added to condense steam, lbs.
180# at 148° F.	163	28.5	30
21.5 at 122		21.5	25
26.5 at 125		26.5	
23.5 at 130		24.5	
22.7 at 135		22.7	
29.0 at 136		29.0	
26.0 at 140		26.0	
26.5 at 142		26.5	
27.0 at 133		25.5	
29.0 at 142		27.0	
		29.0	
		30.0	
		24.5	
		36.0	

Average steam pressure, lbs.—

Gauge	7.3
Corrected	8.7
Absolute	23.4
Latent heat of vaporization at 23.4 lbs., B. T. U.	953.3
Temperature of steam at this pressure, degs. F.	236.0
Quality of steam, per cent.	95.0
Temperature of exhaust steam, degs. F.	151.0
Gross weight condensed steam, lbs.	377.2
Water added	55.0
Net weight of water.	322.2
	B. T. U.
Heat given by steam cooling from 236 to 151 or 85° F.:	
32.2×85	2,740
Heat given up by steam in condensing:	
322.2×0.95×953.3	291,800

Total 319,200

Average vacuum in evaporator—

Gauge, ins. hg.	23.3
Corrected, ins. hg.	23.0
Absolute, lbs.	3.5
Latent heat of vaporization at 3.5 lbs., B. T. U.	1,009.0
Temperature of steam at 3.5 lbs., degs. F.	147.7
Water added, lbs.	411.7
Water left, lbs.	163.0
Water evaporated	248.7

Heat to raise added water to boiling point:

B. T. U.

180# at 148° F., 180×0.3	54
21.5 at 122, 21.5×25.7	553
26.5 at 125, 26.5×22.7	603
23.5 at 130, 23.5×17.7	435
22.7 at 135, 29×12.7	370
29 at 136, 22.7×11.7	244
26 at 140, 26×7.7	170
26.5 at 142, 26.5×5.7	160
27 at 133, 27×14.7	390
29 at 142, 29×5.7	180

3,160

Heat to vaporize water:

248.7×1,009 250,900

Total 254,000

Efficiency, 79.5 per cent.

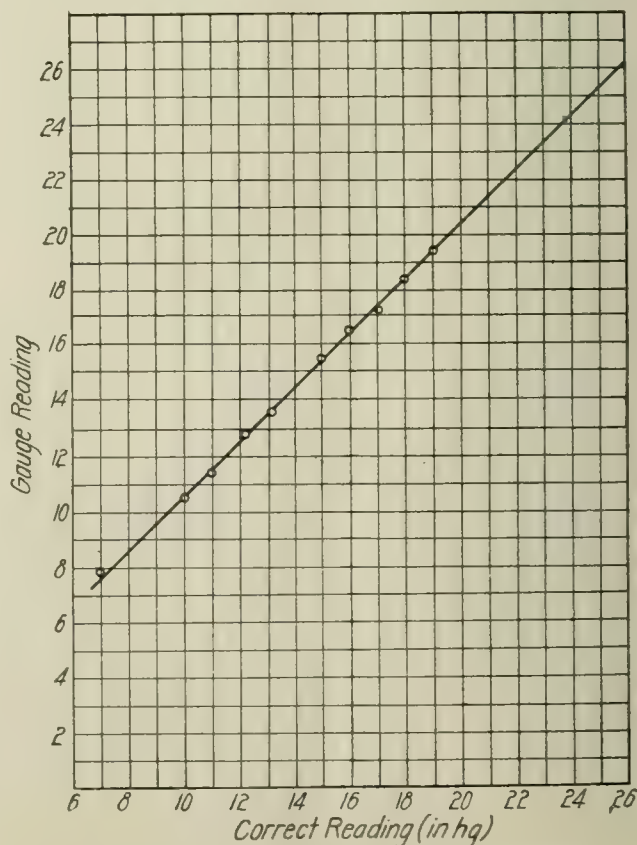


Fig. 4—Curve for Correcting Gauge Readings.

The average results of this series of tests may be summed up as follows, copper tubes, efficiency 83.4 per cent; steel tubes, efficiency 79.5 per cent; tin tubes, efficiency 76.7 per cent, and lead tubes, efficiency 78.8 per cent. With the copper tubes, one of the runs gave an efficiency of 85.2 per cent, much above the average of the other two runs. This was thought to be due to a leak in the steam connections which allowed a small quantity of steam to mix with the water in the

greater. It may also be noted in this connection that the exhaust steam came out at a lower temperature in the case of the lead tubes, than of the tin. Unless there is some unknown error in these determinations we are unable to account for these facts.

In general, it may be said that there is very little difference in the efficiencies for the various tubes, the maximum difference being 6.7 per cent. This is doubtless due to the fact that, with tubes of this small thickness the coefficient of heat transmission does not materially affect the efficiency. This figure may be altered one way or the other, by changing the velocity of the steam, as the first runs made show. These runs were not recorded as the evaporator was not run at anything near its capacity. In the recorded runs the steam velocity was kept as near the same as possible by a proper regulation of valves.

It is planned to continue this study using tubes of the same metal, but with varying thickness, also to carry on a series of experiments with steam at varying pressures and with a varying vacuum.

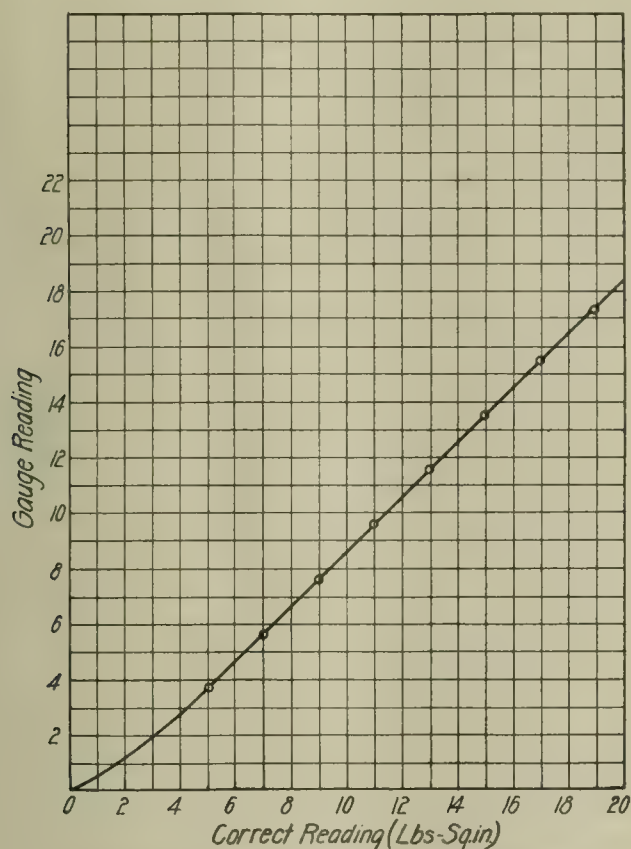


Fig. 5—Curve for Calibrating Pressure Gauge.

evaporator. At the close of this run, the end plates were taken off and the cast iron plates holding the tubes tightened. In the next run, the efficiency dropped to the lower value.

From the above results it may be seen that the efficiency is highest for the copper tubes and next highest for the steel tubes. These results would be expected, inasmuch as copper and steel have a higher coefficient of heat transmission than the other materials used, and also from the fact that the copper and steel tubes were from one-third to one-fourth as thick as the other two sets of tubes. The difference in the efficiency of the copper and of the steel is not as great as might be expected from the difference in their heat conductivities. This is, doubtless, due to the fact that both tubes were very thin.

The relation of the efficiencies of the lead and tin tubes are somewhat harder to explain. Although the coefficient of heat transmission for tin is greater than that of lead, and although the lead tubes were about one-eighth thicker, the efficiency of the latter is

WELSH TIN-PLATE TRADE DIFFICULTIES.

The recent coal strike in Great Britain caused great damage to the tin-plate export trade of Swansea, according to a U. S. Consular Report. The exports of tin plates for May, 1912, show a total of only 23,986 tons, a loss of 18,775 tons compared with the same month of 1911. Swansea has lost not only its entire export trade of tin plates to the United States but many of its important markets, especially in the Far East, where the Welsh tin plates were in competition with the American product. These losses may be seen from Table I of exports:

Exported to—	May, 1911. Tons.	May, 1912. Tons.	First 5 months, 1911. Tons.	First 5 months, 1912. Tons.
United States.....	3,572	37	11,941	740
Canada	920	307	5,538	3,529
China	1,112	405	8,995	2,992
Japan	1,733	692	11,589	9,593
East Indies.....	3,605	2,739	27,066	17,951

The exports to Russia, Norway, France, Roumania, and Australia still show increases, while there are slight decreases to Argentina, Germany, Netherlands, and Italy.

Following close upon the severe blow to the principal industry of this district comes a stike of the transport workers, in consequence of which the docks of this district are entirely idle.

In the warehouses of the Swansea dock and in stock there is a larger supply of tin plates than ever known in the history of the port. This record increase in stock is due to the loss of markets as well as to the congestion in shipping following the resumption of work in the coal mines. The present stagnation in the shipping trade of this port will no doubt tend to lose further markets to the Welsh tin-plate trade.

THE CEMENT INDUSTRY IN 1911.

The statistics of cement production in 1911, prepared by Ernest F. Burchard, of the United States Geological Survey, show an increase over 1910 of only about a million and a half barrels. The increase in quantity is the smallest recorded within the last 13 years, and the fact that the total value showed an actual decrease indicates that trade conditions were not as satisfactory in 1911 as in 1910.

Production of All Cements.—The total quantity of Portland, natural and puzzolan cements produced in the United States during 1911 was 79,547,958 barrels, valued at \$66,705,136. Compared with 1910, when the production was 77,785,141 barrels, valued at \$68,752,092, the year 1911 showed an increase of 1,762,817 barrels, or 2.27 per cent in quantity, but a decrease of \$2,046,956, or 1.48 per cent in value.

Portland Cement.—The total production of Portland cement in the United States in 1911 as reported to the United States Geological Survey, was 78,528,637 barrels, valued at \$66,248,817. This quantity reduced to tons is equivalent to 13,321,822 long tons, valued at \$4.97 per ton. As compared with the production of Portland cement for 1910, which was 76,549,951 barrels, valued at \$68,205,800, the output for 1911 represents an increase in quantity of 1,978,686 barrels, or 2.58 per cent, and a decrease in value of \$1,956,983, or 2.87 per cent. The average price per barrel in 1911, according to the figures reported to the Survey was a trifle less than 84.4 cents, as compared with 89.1 cents in 1910. In the average price for the country is included the value of 135,775 barrels of white Portland cement which sold at an average price of about \$2.50 per barrel.

Prices of Cement.—According to reports made to the United States Geological Survey by the manufacturers the average price of Portland cement per barrel by districts in 1911 in bulk at the mills ranged between 71.5 cents in the High district, and \$1.406 on the Pacific Coast, as compared with 72.9 cents and \$1.385 for the same districts in 1910. The average price for the whole country was 84.4 cents a barrel. The lowest individual average price reported to the Survey was 60 cents per barrel, and many mills sold cement as low as 65 to 67 cents, not only in the East but in the Middle West. The highest figure reported was \$1.70 per barrel from a plant in the Rocky Mountain district.

The year opened with the prices on the downward grade, and there were only temporary revivals. Taken as a whole and judged by the personal testimony of representative cement manufacturers from all states east of the Rocky Mountains, prices appear to have been very unsatisfactory.

Nine New Plants Begin Operations.—In 1911, 115 plants reported a production of Portland cement as compared with 111 plants in 1910. The total number of rotary kilns in the producing plants was 916 as compared with 902 in 1910. These kilns ranged

in length from 40 to 240 ft. The kiln lengths were as follows: 40 to 60 ft., 208 kilns; 60 to 90 ft., 149 kilns; 100 ft., 84 kilns; 110 ft., 140 kilns; 120 ft., 86 kilns; 125 ft., 163 kilns; 125 to 140 ft., 60 kilns; 150 ft. or more, 26 kilns.

The gains were all in kilns 100 ft. or more in length and these gains more than balanced numerically the smaller kilns, which were shut down, giving a total of 559 kilns 100 ft. or more in length in 1911, as against 473 kilns in 1910. The 125-ft. kiln is apparently still the most common length for modern kilns. From the reports received it is apparent that the total annual kiln capacity of the country in 1911, allowing for reasonable loss of time for repairs, should have been about 112,500,000 barrels, and that the total production of 78,528,637 barrels represented about 70 per cent of the total capacity. As compared with the estimated total kiln capacity in 1910, which was 97,670,000 barrels of Portland cement, the capacity in 1911 increased 14,830,000 barrels, or far in excess of the actual increase in production. The apparent average output per kiln in 1911 was about 85,730 barrels, as compared with 84,867 barrels in 1910. This increase is explained by the greater average size of the kilns operated during 1911.

Cement Specifications.—A committee composed of Government engineers and representative consumers and manufacturers, and of the national engineering societies, has recently formulated a set of specifications for Portland cement, to be used by all departments of the Government. The specifications have been published in this journal.

UTILIZATION OF ATMOSPHERIC NITROGEN.

The Bureau of Manufacturers has just published a monograph by Consul Thomas H. Norton, of Chemnitz, Germany, entitled "Utilization of Atmospheric Nitrogen." The consul has been on special detail for the Department of Commerce and Labor. For many years the world has been dependent on the nitrate beds of Chile for supplies of combined nitrogen, and as these beds are not particularly extensive and as the demand for combined nitrogen by the manufacturing and agricultural interests is rapidly increasing, serious efforts have been made to discover new deposits, and many prominent chemists have endeavored to perfect processes for utilizing atmospheric nitrogen. The monograph describes in detail the results obtained by the foremost European chemists, and the commercial as well as the technical aspects of the new industry are dealt with at length. The subjects handled are the present supply of nitrogen, the synthetic production of ammonia, the synthesis of nitric acid, hydrocyanic acid, cyanides, nitrides and calcium cyanamide from atmospheric nitrogen, and coal waste and peat as sources of ammonia. The monograph may be obtained upon application to the Bureau of Manufactures.

A NEW METHOD FOR TESTING PAINT FILMS AND PRESERVATIVE COATINGS FOR IRON AND STEEL.*

By W. C. SLADE.

In view of the difficulty in obtaining trustworthy results concerning the protective values of paints or paint films by tests conducted in the laboratory, any new laboratory method is thereby apt to be received with more or less skepticism. It is believed, however, that the method herein proposed is entirely sound in principle; and it has produced results that demand at least thoughtful consideration. It is further believed that a little more experimentation will make the method suitable for use generally. A report of the work is given at this time inasmuch as experiments related to the test have been carried on at different times for the past two or three years in the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology, and only the very preliminary experiments have been published.

It is not intended to do the impossible in proposing a test that will at once determine the value of a paint from all points of view or under all conditions. In fact, those tests that have been used previously, or are now in general use, are all more or less limited in that they consider only certain ones of the many properties desirable in any paint film. A paint for any particular purpose should always be selected because of particular properties it possesses that other paints do not possess to the same degree. That method of testing should be used which considers most prominently those particular properties.

Unfortunately, many tests are conducted under abnormal conditions, and results thus obtained are not necessarily identical with those that would be obtained under normal or actual conditions. Thus, the Loesner steam test,¹⁻² the electrical insulation or voltage test¹⁻² the heat test (2 hours at 400° F.),² and tests where films are subjected to the action of weak acids or other attacking agents are either unnatural in themselves or are performed under unnatural conditions. Of course some of these tests are directly applicable and desirable provided the paints are to be used where steam or acid fumes prevail, or on surfaces subjected to heat, etc. Some tests eliminate the vehicle, and too often the tendency is to predict the behavior of paint films from the results of experiments carried on with the pigments contained in the films. The vehicle is too important a part of a paint to neglect. The Cushman knife blade test,¹ or Perry damp film test,¹ and the Thompson test³ are all tests performed on the pigment alone. Nevertheless, both of these tests have produced most interesting results with commercial pigments, and it is to be noted later how closely the results, particularly of the Thompson test, agree

with the results obtained by this new method. The differences noted are undoubtedly due largely to the fact that this method shows more than the Thompson method, in that it is a test for pigment and vehicle combined. It will be shown later how in certain cases the properties of a paint film may obscure the property of the pigment (as determined by the Thompson test) contained therein. One of the early tests was the evaporation test.¹⁻² An iron dish painted on the inside is filled with water which is allowed to evaporate. The dish is repeatedly refilled after each evaporation until the paint film has deteriorated, or until the time of the test has extended sufficiently. From one point of view, the alternate wetting and drying periods represent the wet and dry conditions in a painted surface exposed in actual service. An acceleration test by Norton¹ involves the principle of alternate wetting and drying, but is entirely qualitative in character. The Garner acceleration test¹ is also a qualitative one and provides for subjecting small painted test plates to artificial atmospheres. Recently, a test has been proposed by Benson and Pollock,⁴ which is a sort of electrical insulation test carried out in a normal salt solution, wherein the film surfaces are subjected to a potential difference of 8 volts. There are a few other tests that have been proposed from time to time to determine specific properties of paint films, such as hardness, elasticity, porosity, etc., the majority of which may be found described in the bulletins of the Paint Manufacturers' Association of the United States.

The ideal paint film would be not only uniform and tough and adhere well to the surface beneath, but would be at the same time sufficiently elastic to prevent cracking, and quite impervious to destructive gases and liquids. If it be a case of protecting iron and steel against corrosion by means of a paint film, imperviousness to moisture and to air or to oxygen is the property most essential. This new method determines the degree of imperviousness or the excluding power, and allows all results to be recorded permanently and to a certain extent quantitatively. It utilizes the principle of alternate wetting and drying, and works under conditions made to imitate actual conditions as far as possible.

DEVELOPMENT OF THE METHOD.

The method has its origin in the results of experiments with fruit-can lacquers performed by Walker and Lewis⁵ in 1909, when it was shown why lacquered cans when filled with fruit juices rusted more rapidly on the inside than unlacquered cans when filled. The apparatus used was later utilized to experiment with several paint films. It consisted of a U-tube, 1 in. in diameter, which contained 200 cc. normal KCl. Each arm contained a spiral of soft iron wire, and containing 25 cm. of wire, the other 100 cm., and both spirals were immersed in the electrolyte. The

*From the Journal of Industrial and Engineering Chemistry. ¹Gardner and Cushman, "The Corrosion and Preservation of Iron and Steel," pp. 241-243.

²Gill and Foster, Tech. Quarterly, 17, 145 (1904).

³Thompson, Trans. Am. Soc. Testing Materials, 7, 493 (1907).

⁴Benson and Pollock, Journal of Industrial and Engineering Chemistry, 3, 9 (1911).

⁵Walker and Lewis, Ibid., 1, 11 (1909).

longer spiral bore the dried coat of paint to be tested. The solution around the spiral was kept saturated with air by constantly bubbling a stream of air through it. The two spirals were connected through an external circuit in which was placed a bromide coulometer. An electric current developed sooner or later at the painted spiral, resulting from the depolarization of hydrogen ions by the oxygen, and the quantity of electricity developed was determined in the coulometer. The weight of bromine added per unit time may be considered as a measure of the rate of depolarization. The theory of the process will be considered more in detail later. For later reference, a few measurements obtained are given here. The films that depolarized the least head the column. The thickness of the films was not measured.

Coating.	Br. per hour, mg.
Paraffine	0.00
Zinc oxide.....	0.078
Graphite (baked).....	0.078
White lead.....	0.10
Zinc chromate.....	0.11
Barytes	1.2
Graphite	1.87
Lampblack	2.3
Carbon black.....	2.4

The work was now taken up by M. T. Jones who experimented with a number of paint mixtures and used the bromide coulometer to record the various rates of depolarization. The use of the coulometer was later discontinued, however, as its resistance in the circuit during the course of a long run increased greatly, so that the quantity of electricity allowed to pass continuously fell away from that quantity which would have passed, had the resistance of the coulometer remained constant. For this reason, the results obtained with the coulometer are not given at this time. Jones next measured electromotive forces by means of the Poggendorf compensation method, but it proved too tedious and not sufficiently productive to warrant its continuance. Direct measurement of current was then attempted with the use of a specially constructed milliammeter and a few trials produced excellent results. Jones did much towards standardizing the method, and had constructed an apparatus which was at first used to allow for wetting and drying periods when his untimely death occurred. The following year the apparatus was improved and greatly extended, and the investigation continued by the writer.

THEORY OF THE METHOD.

A brief statement of the theory of the method which involves the electrolytic theory of corrosion follows: Consider two identical pieces of iron immersed in water, containing a dissolved neutral electrolyte to give conductance, and connected through an external circuit. No current can pass through the external circuit in either direction, for identical conditions of equilibrium obtain at each metallic surface, and will obtain until this equilibrium is disturbed at one of the electrodes. By removing hydrogen ions at the surface of the electrode, as can be done by depolarizing with

a steady stream of oxygen, the equilibrium can be constantly disturbed. At the same time an electric current passes continuously through the circuit. To maintain the equilibrium of ionic charges within the solution, metallic iron must pass into solution at some point in the form of ferrous ions. This takes place almost wholly at the undepolarized electrode. Of course water is the product of the depolarization, and the ferrous ions unite with the hydroxyl ions (which are chemically equivalent to those hydrogen ions removed) to form ferrous hydroxide, which in turn is oxidized to the ferric form and to insoluble rust. A rust coating forms at the depolarized electrode or cathode and so some iron must be going into solution

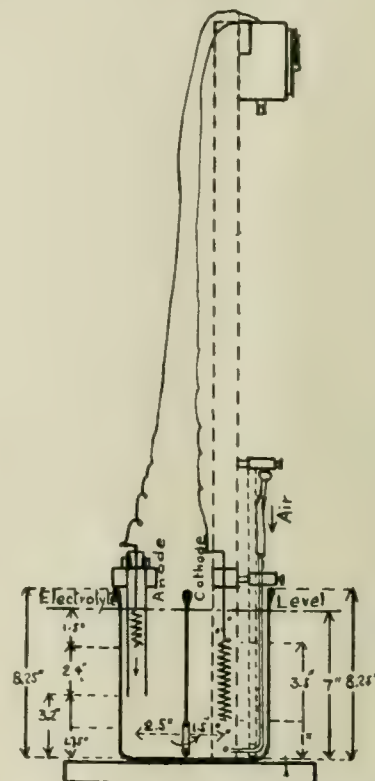


Fig. 1—Cross Section of Paint Cell No. 1.

here; but it is only a few per cent of that moved into solution from the other electrode or anode. The cause for this probably lies almost wholly in local action on the cathode, for practically no depolarization takes place at the anode.

Let the electrodes be in the form of spirals of iron wire and the electrolyte consist of normal KCl; and consider the cathode spiral to be covered with a well dried coat of paint and the solution around it to be continuously saturated with air. The combination of painted spiral + electrolyte saturated with air—bare iron spiral + electrolyte containing no air will be called for convenience a "paint cell." The paint film may or may not electrically insulate the cathode wire. Probably every paint is porous at least to some extent, so that it is only a question of time as to how long it will require for the solution to penetrate the film sufficiently to establish contact with iron at one or more points. When this occurs, the hydrogen ions that

tend to polarize are depolarized by the oxygen of the air which is in solution, and the operation of the paint cell commences. Though the driving force of the reaction is not affected by the presence of the film, the rate of reaction or depolarization is greatly affected. The initial current detected is very small—a few thousandths of a milliampere—because of the great resistance offered by the film, not only to the passage of a current but to the diffusion through the pores of the film of the air. With increased porosity comes an increased rate of diffusion and an increased rate of depolarization and a decrease in film resistance. The current consequently increases. At this time any depolarizing power possessed by linoxyn⁵ that may still be unsaturated to a certain degree should show its influence. The relation between the rate of diffusion through the film and the rate of depolarization was well illustrated by an experiment where several coated spirals, with films slightly disintegrated, were supplied, first with excess air and then with excess oxygen gas. In the second instance the current values more than doubled, returning again to the original values when air was resubstituted.

The relative behavior of films made from different kinds of paints indicates the relative excluding powers to moisture and oxygen. The increase in current observed in any paint cell may be recorded in a current-time curve giving a permanent record of the behavior of the film.

It is interesting to note the analogy between the arrangement of the paint cell and the conditions existing on a painted surface, injured with scratches or bare spots, of any portion of an exposed steel structure. Assuming the injured surface to be covered with dew or rain water, then the bare spot or scratch, the protected or painted surface around the injury and the water covering both correspond respectively to the anode, cathode and electrolyte of the experimental paint cell. Of course, in this case the rate of depolarization would be less and the resistance to passage of current through the liquid circuit much greater than in case of the paint cell, but the process would proceed definitely and steadily, notwithstanding.

To allow alternate wetting and drying, that actual weather conditions might be approximated, the apparatus described below was finally adopted.

THE APPARATUS.

The apparatus consists of five identical units, each unit having a testing capacity of 14 painted spirals. Each unit includes an electrolyte tank measuring approximately $28\frac{1}{2}$ in. $\times$ $6\frac{3}{4}$ in. $\times$ $8\frac{1}{4}$ in., filled to a depth of 7 in. with normal KCl solution. A metal partition with a cloth diaphragm of a width of $1\frac{3}{4}$ in. along the bottom divides the tank longitudinally into two sections. The tanks and partitions are made of galvanized iron well coated on the inside with an asphaltum paint. At the back of each tank is a series of 14 tubes, closed tightly at the top with corks and wax, and extending below about 4 in. into the KCl

solution. Each tube contains one bare iron anode. There are also 14 cathode spirals which are held in a frame that is free to slide up and down in guides, thus permitting the spirals to be removed for periods of drying when desired. The tank is so placed that the cross-sectional dimensions of any individual paint cell is as represented in Fig. 1.

The air is supplied by tubes held in position by a frame which can be so adjusted that each tube can deliver a stream of air bubbles directly up through a cathode spiral. This insures the continuous saturation of the solution in the immediate vicinity of the electrode. On the other hand, the anodes are so placed and so shielded from access of air (except that small amount which may diffuse down through the solution and up inside the tubes) that the oxygen content within the anode tubes is practically depleted all the time.

Each cathode is connected to its corresponding anode through an external circuit. The connections are all made in a switch-box in such a manner that when the paint cells are working, each cell sends its current through an individual 100-ohm resistance coil; and when measurements are to be made, and a milliammeter with an internal resistance of 100 ohms has been connected to the binding posts of the box, then, by moving a radial contact arm, the current from any individual paint cell may be sent at once through the 100-ohm coil of the milliammeter instead of through its 100-ohm coil in the switch-box. Each paint cell is entirely distinct from its neighbors. The 14 paint cells have only the electrolyte in common. The use of the resistance coils makes it possible to read directly the current that is actually passing when the milliammeter is thrown into circuit.

The resistance coils are made of No. 36 German silver wire and are wound on glass tubes which in turn are inserted into small 3 in. weighing tubes closed at the end with sealing-wax. They were checked against a standard when made and are correct to within 1/5 per cent.

The air, supplied by a small motor-driven rotary blower, passes first into an equalizing chamber and then into the main distributing pipe. The supply is steady and regulated to about $1\frac{1}{5}$ - $\frac{1}{4}$ cubic ft. per minute per tank.

The wetting and drying periods are controlled by clock work. The hour hand of the clock makes contacts at desired intervals such that electric circuits are made. A relay is thereby brought into play and a larger current passes through a motor which controls the raising and lowering mechanism of the cathode frames. According to the particular contact that the hour hand makes, the frames are raised or lowered. For tests recorded in this paper, the wiring was arranged to give lifting contacts at 3, 6, 9 and 12 o'clock and lowering contacts at 1, 4, 7 and 10 o'clock. There were thus 8 one-hour drying periods and 8 two-hour wetting periods per 24 hours.

The spirals are made of a soft iron wire, No. 19,

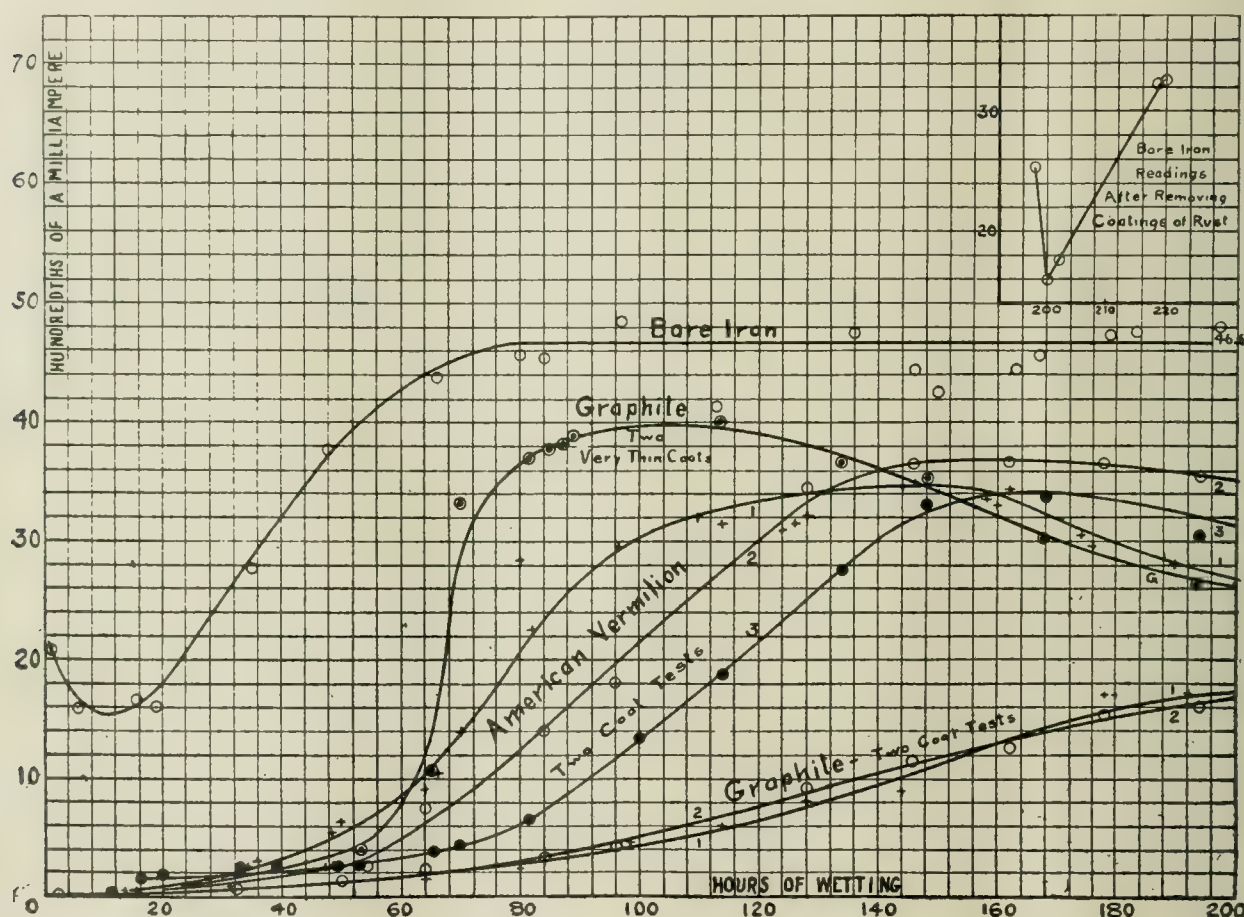
U. S. standard, and wound in a lathe on a $\frac{3}{4}$ in. lag screw having $4\frac{1}{2}$ threads per inch. The electrodes are so wound that when in proper position exactly 100 cm. of the cathode wire and 25 cm. of the anode wire is under the solution. All spirals are cleaned by picking in dilute sulphuric acid. They are then carefully washed with water and dried with alcohol or ether.

CONCERNING THE PAINTS AND PAINT FILMS TESTED.

To determine as far as possible the value of the apparatus, paint mixtures were made from ten representative commercial pigments, some of which are recognized as good, and some as poor paints, according to the point of view. The pigments were kindly furnished by the Paint Manufacturers' Association and

lead, iron oxide, barytes, silica, carbon black and natural graphite. Now the fineness of a pigment determines the thickness of the paint film. Whether or not the various mixtures were of comparable viscosities, several of the paints when applied in coats at all thick tended to slide off from the wire. This was the case with the paint made from some of the more coarsely ground pigments. The difficulty was obviated to a great extent, however, by the method of drying the films.

The carefully cleaned cathode spirals were coated by dipping into the well shaken paint mixture. The excess paint was allowed to drain until dropping began and the spirals then transferred to a drying wheel. This consisted of a wooden wheel about 2 ft. in diam-



Plot I.

came in paste form, ground in pure, refined linseed oil. In each case they were thinned to the desired viscosity with a mixture by volume of $\frac{2}{3}$ pure raw oil and $\frac{1}{3}$ oil of turpentine. The amount of oil used in grinding each pigment, and the amount of vehicle used for thinning each, is on record. The object was to obtain a fairly rapidly drying paint mixture that would be of a viscosity not far from that desired for practical application, and at the same time be of such a nature that fairly thick and very uniform coats could be obtained on the iron spirals. Herein lay a difficulty. The paints investigated were zinc oxide, zinc-lead chromate, American vermilion, red lead, white

eter, slowly rotating in a vertical plane. Its face was divided by partitions into eight compartments, each compartment enclosing a number of holes drilled into the face of the wheel. The ends of the coated spirals were inserted into the holes in such fashion that the spirals turned with the wheel, thus permitting the fresh paint to flow around the wire rather than drain away in drops. Eight different paints could be dried at one time. When sufficiently tacky, the spirals were transferred to a window with western exposure for thorough drying.

The magnitude of the variations in thickness of the films can be best represented by giving a few measure-

ments made by calipering two coat films. The coats, as a rule, were fairly uniform, but variations up to 20 per cent occurred at some places.

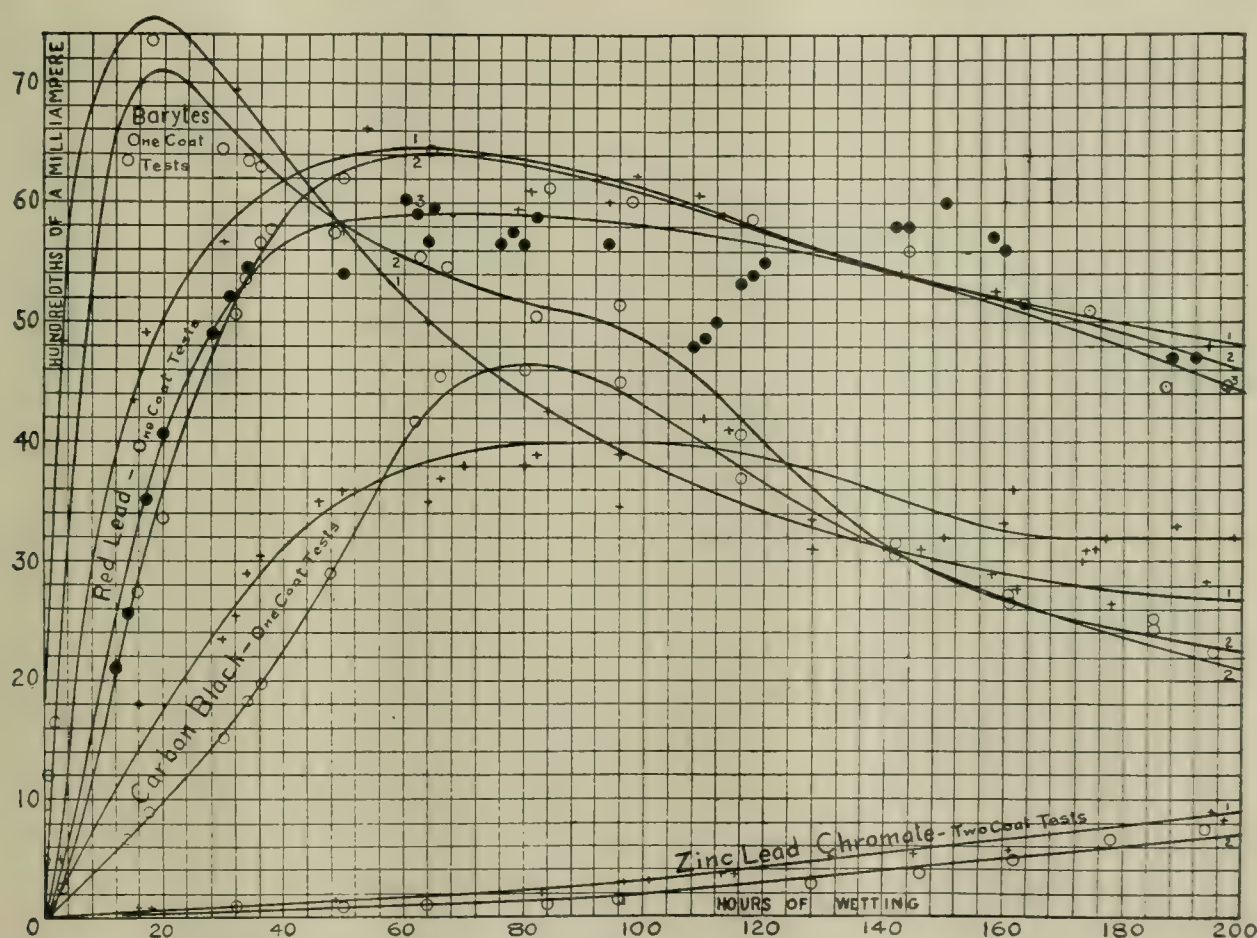
Average thickness.
(Several readings.)

Paint.	Test I. mm.	Test II. mm.
3 American vermilion.....	0.09	0.09
7 Barytes	0.09	0.09
4 Red lead.....	0.10	0.09
5 White lead.....	0.10	0.08
6 Iron oxide.....	0.10	0.07
8 Silica	0.10	0.09
9 Carbon black.....	0.13	0.12
1 Zinc oxide.....	0.14	
2 Zinc-lead chromate.....	0.14	
10 Graphite	0.14	

When spirals were given a single coat, the time for

readings are averaged. It is this average that determines a point for a current-time curve, one of which is drawn for each test, and which is so drawn as to be the most representative curve. Most of the tests were extended over a period of 300 hours of wetting, but it appears that 200 hours, and perhaps even 150 hours, is quite sufficient. The thickness of a coat or the number of coats really determines the time required. On Plots I. and II. are given several curves together with the experimentally determined points.

With each one of the ten paint mixtures two one-coat tests and three two-coat tests were carried out, excepting zinc-lead chromate, zinc oxide and graphite, where only two-coat tests were finished. From the



Plot II.

drying varied from 2-3 weeks. In case of two coats of paint, the first coat dried 3 or 4 days and the second coat 2-3 weeks, except that films in the first series dried about a month.

METHOD OF TESTING AND TREATMENT OF DATA.

For each separate paint test three spirals are coated simultaneously and dried for the same period of time. They are then properly adjusted in the cathode frame and connections from the switch-box made by soldering. Air is then bubbled through the solution, and at the proper time the first immersion begun. Current readings are taken at the start and after this at the end of each two-hour wetting period. Unless one value chances to be considerably in error, the three

curves determined as described above, in only one case, the one-coat tests with white lead, was there wide divergence between the two curves; with the exception of a few cases of only fair agreement, the several runs checked up very well. Referring to Plots I. and II., the curves for all the paints but American vermilion are examples of the generally good agreement obtained. The character of the checks among the American vermilion curves is typical of the less accurate checks obtained in the cases of only fair agreement, such as the two-coat tests of red lead, white lead and iron oxide. It was almost impossible to get a good, uniform coating of white lead of the desired thickness—such that it would be comparable with the thickness

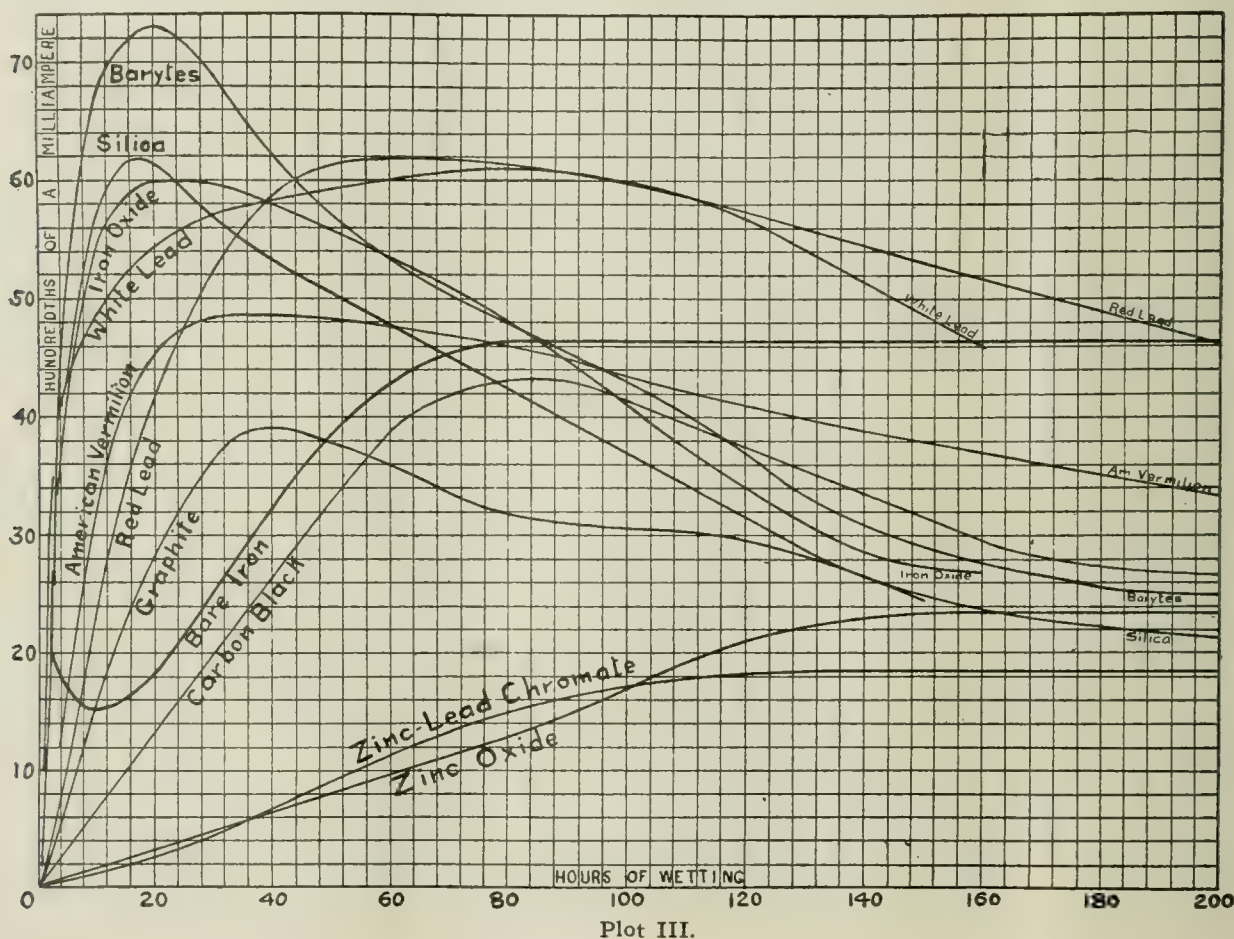
of the other films. To this fact may be traced the cause of the great disagreement between the white lead tests, and the smaller disagreements in a few of the other tests. On the whole, all the paints considered, the several runs check among themselves very well. The spirals for the several series of tests were coated and dried at different times, with the periods of drying varying somewhat, necessitated by the lack of time. Besides, the several series of tests were carried out in different tanks and at different times, thus giving all opportunity for disturbing factors to appear. It is impossible to include all the preliminary curves because of the space required.

In order to bring the results together in comparative relationship, Plots III. and IV. have been prepared.

only great enough to account for but a small part of the wide divergence from one another of the finally determined mean curves. Aside from influence of thickness, which is directly related to excluding power, is to be considered the influence of the depolarizing property of the film. It appears that this is more a property of the film; as a whole, than a property of any constituent part of the film. Both factors are to be considered more fully.

INTERPRETATION OF THE CURRENT-TIME CURVES.

On Plots I., III. and IV. appears a curve called the bare iron curve. This was determined by making a run with fourteen carefully cleaned bare iron cathodes exactly similar to those used in the paint tests. The points locating the curve are shown on Plot I. At



Each curve on both of these plots is drawn from data obtained from the various best representative curves of the individual tests by averaging these curves. Each curve on Plot III. is determined by the position of two of the one-coat test curves; those on Plot IV. by the positions of the three corresponding two-coat test curves. Both sets of curves are discussed later. It may be noted here, however, that the increased protection of the two coats over the one coat of each paint shows up well; also that the relative position of the curves on both plots is in general the same. It will be remembered that the film of zinc oxide, zinc-lead chromate, carbon black and graphite were slightly thicker than the other films. But the difference is

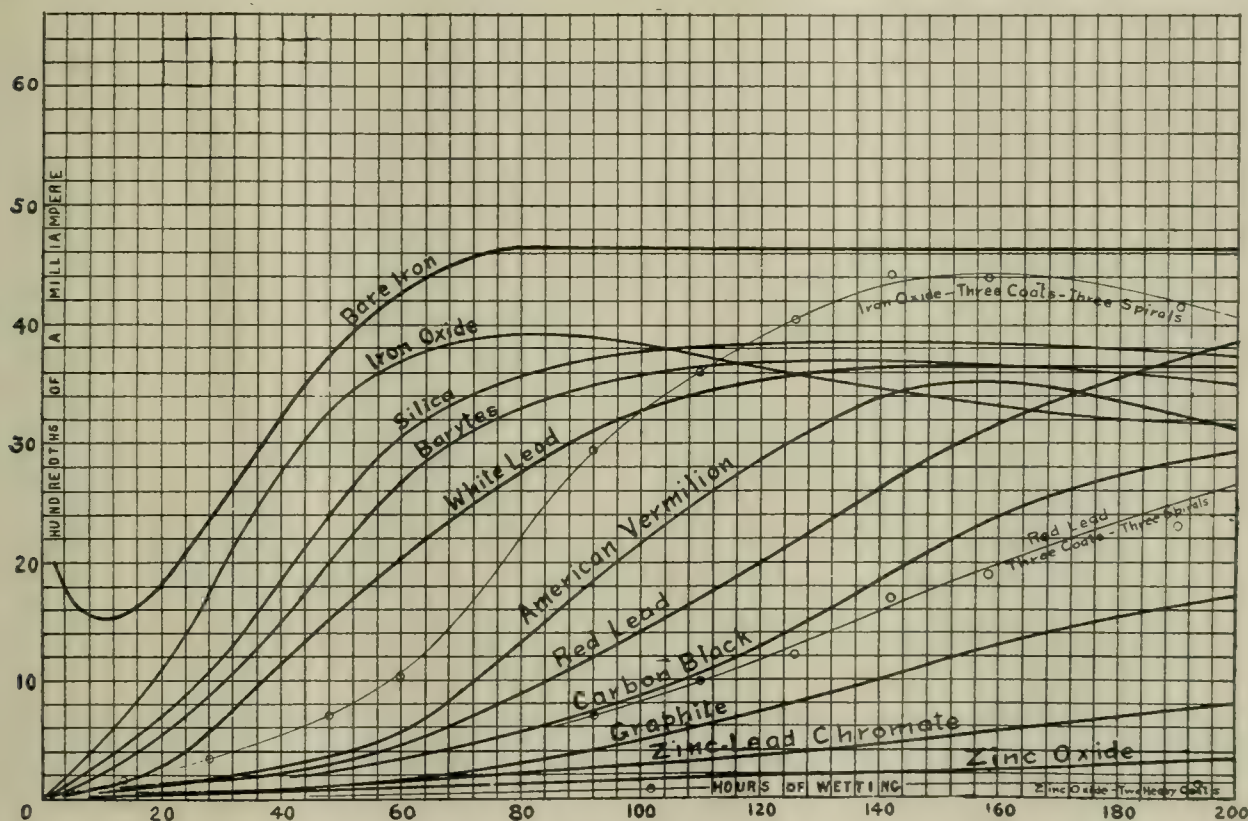
the start of the test with no rust on the spirals the current was about 0.20 milliampere. As a thin rust film formed, either the resistance must have increased or the electromotive force decreased, for at 10 hours of wetting a minimum value of about 0.16 milliampere was reached. Beyond this point the current rapidly increased until a constant value of 0.466 milliampere was reached. This period of increase marks also the period of rapid accumulation of a rust coating. At the end of 197 hours of wetting, the accumulated rust, which acted as a spongy envelope about the wire, was carefully removed, and the run again continued. The current immediately fell to about 0.25 milliampere and, as previously, strangely enough passed through a min-

imum before rust formation caused another rise. The increase in current was concomitant with the increase in depolarizing power of the coating. Within the spongy envelope the rate of the union of hydrogen and oxygen was increased. For the first few hours of wetting, the quantity of rust formed is not sufficient to exert its influence in this direction.

The form of the curves of the one-coat paint tests shows that, in several instances, marked depolarizing power is acquired soon after the films begin to disintegrate sufficiently to allow a more rapid absorption of solution and air. Maxima of current values are reached far above the value given by a bare iron cathode when heavily covered with rust. With the

curve is given which bears out the argument. In this case spirals covered with two very thin coats were used. Up to 50 hours of wetting the excluding power was excellent, but then this decreased very rapidly indeed, and so the rate of depolarization in the film increased accordingly. The maximum is the same as that reached in the one-coat test for graphite on Plot III. Graphite and carbon black are recognized most generally as good excluders, graphite because of the unctuous nature of the pigment. The danger in their practical use lies in getting coats too thin.

Barytes and silica paints are not good excluders, and these pigments are always used as fillers in other paint mixtures. These paint films possessed the poorest ex-



Plot IV.

two-coat curves the maxima are less pronounced or even do not occur at all.

Evidently there are two distinct effects that tend to overshadow each other: that of depolarization, which is most pronounced in thin coats that disintegrate easily (and so acquire high powers of absorption), and the effect of exclusion or imperviousness, which increases as the thickness of any coat or the number of coats is increased.

It is interesting to note that zinc oxide, zinc-lead chromate, carbon black and graphite appear as the best excluders. But given a film sufficiently thin, such that the depolarizing effect may become prominent, then it is again to be noted that while zinc oxide and zinc-lead chromate do not increase the rate of depolarization, carbon black and graphite do increase the rate of depolarization. On Plot I. another graphite

cluding powers and the highest depolarizing powers in the one-coat tests, and next to the poorest and highest in the two-coat tests.

Iron oxide from one and two-coat tests appears to be not only a poor excluder but a strong depolarizer. The three-coat curve inserted on Plot IV. confirms this, representing less protective value than that afforded by two coats of American vermilion. It is also noticeable that the three-coat curve for red lead, though lying decidedly below the two-coat curve, still lies above the two-coat curves for zinc oxide, zinc-lead chromate, and graphite. Unfortunately the white lead curves (and to some extent the red lead curves) are not determined as accurately as the others. It appears, however, that red lead has better excluding power than white lead, but both films exert equally high depolarizing power. Both red lead and American ver-

million give fair excluding power. The lowest curve of Plot IV. for zinc oxide represents two-coat tests wherein the films were thick enough to equal very closely the thickness of those films of the three-coat tests of iron oxide and of red lead. The differences in excluding and in depolarizing power is marked.

The first experimental results obtained by Walker and Lewis agree with those obtained now, generally considered, for they used films much thinner than those tested here. That is why in their tests carbon and graphite showed up the poorest. It is also interesting to note the relation between the classification of the paint films according to this test, and the classification of the pigments contained in the film according to the Thompson test. As a result of the latter test, Cushman has determined upon calling pigments either stimulators of corrosion, inhibitors or inert (indeterminate) substances. Preserving the order of his listing, a few pigments have been selected from his table, as follows: Inhibitors: zinc-lead chromate, zinc oxide, white lead; Indeterminates: red lead, Princess metallic brown, American vermilion; Stimulators: bright red oxide, carbon black, barytes, graphite. Again excepting carbon and graphite, there is general agreement between the order of the preceding pigments, and the order of the positions of the current-time curves of the paints made from some of these pigments, and tested by the new method.

At the conclusion of tests the disintegrated paint films were often removed to permit the examination of the iron wire beneath. The wire beneath the zinc-lead chromate film was found to be always bright, and without any etching which would result from local action on the electrode. On the other hand, the wire beneath such films as those of barytes, silica or iron oxide was noticeably etched in numerous places. This is in accordance with the view held regarding the inhibitive power of chromates.

The question naturally arises: What causes the current to fall away so rapidly from the high maxima? This is hard to answer. All curves reach values lying between 0.15 and 0.25 milliamperes at 300 hours of wetting, which is far below 0.466—the value for the well rusted bare iron cathode. From the appearance of the spirals at this time it seems very probable that the pores of the films have become choked up with rust. In fact, some of the coats would not be recognized as paint films. Maxima often occur—especially in one-coat tests before the films show decided failure. That disintegration is in progress is evident, however, from the accumulation of very small blisters all over the film surface. At the maxima, the resistance of the film to passage of electricity or oxygen is at a minimum. It may be that, though the resistance to the passage of the current does not decrease very rapidly, the resistance to the diffusion of air does decrease sufficiently rapidly to cause the rate of depolarization to decrease very fast, especially after the most pronounced maxima. The choking of the pores of the

film by even a small amount of rust would account for this.

THE EVALUATION OF PROTECTIVE VALUES.

It would seem most natural to refer all curves to the bare iron curve, calling some value along the curve the value for zero protection. But the curve covers such a range of current values that it is difficult to select any but perfectly arbitrary points. It does not seem justifiable to select 0.466 mg. for the value, as, when this is reached, considerably more rust has accumulated than ever appears on completely disintegrated paint films; nor can a value as low as 0.20 mg. be chosen, as this would greatly undervalue the protection given by all films. Inasmuch as such a method would demand, not only the selection of a perfectly arbitrary point, but a selection that might prove misleading, another method has been adopted.

The curves are current-time curves, and hence the area included between any curve and the co-ordinates corresponding to any point on the curve represents a quantity of electricity. The magnitude of the included area or of the quantity of electricity—in coulombs, for example—is directly proportional to the amount of depolarization that has proceeded up to the same time. The point of time to which to integrate along any curve has been determined in several ways, and thus far no one way has been adopted in preference to the others. The different methods lead to essentially the same results. Thus all areas up to (A) 70 hours or (B) 100 hours of wetting might be integrated; or (C) integrate to the points where the curves pass through some ordinate, as at 0.20 milliamperes. Again, the maxima of the curves might be used as points to which to integrate. In this case, the time at which the maximum occurs must be considered. Let it be assumed that the sooner the maximum occurs the more rapid the deterioration of the films; and the greater the magnitude of the maximum, the greater the depolarizing power of the film which, in turn, depends directly upon decrease in excluding power or increase in deterioration. In other words, deterioration may be represented as directly proportional to the area integrated and inversely proportional to the time or to some power of the time. Protective power may be represented as the inverse of this. Hence, $P = Ct^n/A = Kt^n/Q$, where K is a proportionality constant, t the time up to the maximum current, Q coulombs passed through the circuit up to the time t , and n an arbitrarily chosen constant. Relative values have been obtained by calling K unity and by assigning to the exponent n the value (D) 1 and (E) 2. This method may be used only in case of the one-coat tests. The quantitative results of the above method are, for the sake of brevity, summarized below in a qualitative manner. The capital letters refer to the preceding methods, and the figures to the paint mixtures as follows: (1) zinc oxide, (2) zinc-lead chromate, (3) American vermilion, (4) red lead, (5) white lead, (6) iron oxide, (7) barytes, (8) silica, (9) carbon black,

(10) graphite. The higher the position of a number in any column, the greater the excluding power, and, as a rule, the less the depolarizing power of the paint film.

Two-coat tests.		One-coat tests.			
A, B.	C.	A.	B.	D.	E.
1	—	1	1	2	2
2	—	2	2	1	1
10	10	9	9	10	9
9	9	10	10	9	10
4	4	3	3	3	5
3	3	4	8	4	4
5	5	8	4	8	3
7	7	6	6	6	6
8	8	5	7	5	8
6	6	7	5	7	7

WORK NOT REPORTED.

Although the method uses current values, a large number of electromotive forces were measured, taken after the current readings and after breaking the circuit. Data relative to the change in resistance of the film were thus obtained. Direct measurement of resistance is greatly disturbed by the condenser-like action of the paint films. All this will probably be considered more fully later.

An attempt was also made to determine the cause for certain inexplicable deviations among the average values of the current readings that sometimes occurred during the course of a test. An examination of plots I. and II. shows a few widely displaced points, especially on the third curve for red lead. All conditions were guarded as carefully as possible; the electrolyte was kept at constant level, thus preventing change in conductance due to change in concentration. Temperature changes were watched. The resistance of the electrolyte between bare iron cathodes and anodes was only 18.6 ohms, which formed a part of the resistance of the total circuit of about 119 ohms. This being the case and, further, the temperature changes in the tanks being small, no corrections were made in the current readings. These corrections would have accounted for but a few per cent of the wide deviations referred to above. Except for a few days when the temperature varied $18 \pm 4^\circ$, it varied only $19 \pm 2^\circ$. The change in solubility of oxygen was thus very small, and could not account for the deviations anyway, as they were frequently in the wrong direction.

CONCLUSION.

The work done thus far indicates that the method is sound in principle, reasonably practicable, and reliable, in that under the same conditions of testing, results can be duplicated. It determines definitely, and under artificial conditions made as nearly natural as possible, the excluding power of any paint film against water and air. As regards the testing of paints for use on iron and steel, the method should develop into one of especial value, as the nature of the corrosion through the painted surfaces (according to the electrolytic theory of corrosion) is entirely analogous to the mechanism of the reactions in the paint cell.

It has further been shown that, at least under the conditions maintained in the test—and it is probably true to varying degrees under conditions of actual

service—films prepared from certain of the pigments experimented with possess a marked depolarizing action. This may be in part the saturation of unsaturated bonds in the linnoxyn by addition of nascent hydrogen, as it has been shown that linnoxyn will depolarize hydrogen under the conditions maintained; and it may be due in part to depolarizing properties possessed by the pigments themselves; but it appears that the rate of depolarization is determined largely by the character of the whole film—that is, pigment and vehicle combined. Increasing the porosity or the thinness of a film makes it possible for the depolarizing action to appear, but it apparently does not necessarily cause it to appear. The exact nature of the depolarizing action, and its true relation to the thickness of the film will be investigated more fully in the future.

PURCHASING COAL.

Manufacturers and others who use coal in considerable quantity will be interested in Bulletin 41 of the United States Bureau of Mines, on the subject, "Government Coal Purchases under Specifications." This bulletin, which has just come from the public printer, was prepared by George S. Pope, engineer in charge of fuel inspection for the Government, and contains a chapter on the fuel inspection laboratory of the bureau by Joseph D. Davis, chemist in charge. The bulletin is the fourth of a series showing the results of the purchase of coal by the Government.

Mr. Pope, in his introductory says:

The purchase of coal on the dealer's statement as to quality or on the reputation of the mine or district producing the coal is gradually being discontinued. At present most coal-purchasing contracts make definite provisions regarding the desired heating value of a coal and the composition as shown by the analysis. The heating value is usually expressed in British thermal units and the composition specified is that shown by proximate analysis. The price to be paid for delivered coal is made to depend on whether the analyses and heating value of samples representing the delivery shows the quality to be above or below the quality set forth in the contract.

The replies to a circular letter sent to the mayor of every city of over 100,000 population in the United States brought out the fact that about 55 per cent of the cities replying purchase coal under specifications, many of which are similar to those used by the government. A great many industrial concerns are likewise purchasing coal under specifications. The numerous requests received by the bureau of mines for authentic information concerning purchases of coal under specifications, or according to its heating value, attest the growing interest in the subject.

The purpose of this paper is to explain in general terms the methods that the government has found most satisfactory for the purchase of a large part of its coal supply, including the consideration of bids, the awarding of contracts, and the analyzing of samples on which the price corrections are based.

Copies of this bulletin may be obtained by addressing the director of the bureau of mines, Washington, D. C.

The production of manganese ores in the United States in 1911 was 2,457 long tons, valued at \$24,586. The ore was mined in California and Virginia.

SOME OBSERVATIONS REGARDING GAS OVENS IN EUROPE AND AMERICA.*

Until very recent years there has been little advance in methods of carbonizing coal for the production of gas. About 100 years ago, small quantities of coal, 100 or 200 lbs., were introduced into cast iron retorts and carbonized at a red heat. Forty or 50 years ago, somewhat larger retorts were made from fireclay. The size of the retorts has been increased and temperatures of carbonization have been raised. Some retorts have been placed in a horizontal position, open at one end, and other kinds are open at both ends.

In small works the short retorts are charged with a shovel and the coke drawn by hand. In larger works, with through retorts, the stoking and drawing are both done mechanically. Retorts are also placed in inclined positions to automatically discharge by gravity the coke when carbonized. Recently, vertical retorts of different types have been built and operated on the Continent and in England, and still more recently, through installations have been constructed in the United States.

The tendency has been to increase the heats of carbonization until perhaps 2,600° F. have been reached. The higher heats have had a tendency to slightly increase the production of gas with the retort process, but at the same time this has the effect to decompose some of the lower hydrocarbons in the gas, the formation of naphthalene and the destruction of desirable hydrocarbons in the gas. This carbonization has required from 3 to 6 hours, with a consequent formation of a light, spongy coke. These heats have also produced a high percentage of carbon in the tar. Retorts are oval or cylindrical, and the largest of them would hold no more than 600 to 700 lbs. of coal.

When the charging and drawing are done by hand, the cost of labor is very high and the production per man low. Such labor is exhausting and requires very considerable strength, with the consequence that such labor is hard to secure and rather undependable. This cost and condition of labor have tended to make the manufacture of water gas, in many localities, more desirable, even if it is somewhat more expensive. Mechanical handling of coal and coke, with retort process, has been maintained and improved in many localities.

The construction of by-product coke ovens has pointed the way to carbonize coal at a lower temperature, and in larger bodies, with much less labor per unit. In the by-product process a portion of the gas is used to carbonize the coal. These ovens have led to the construction of ovens heated by coke furnaces or furnaces using producer gas to heat the oven and saving all the gas produced for sale and general distribution. These ovens are rectangular and will contain from 4 to 14 tons of coal each. The process of carbonization is slow, occupying from 16 to 24 hours,

and the temperatures are lower, from 1,900° to 2,100° F., producing a superior quality of coke, more gas to the pound, tar containing less carbon and more ammonia.

There are two or three similar types of gas ovens, of different sizes and positions, now being operated in European countries. It was my privilege to observe and examine these in several different cities of the Continent during the past year. This type of oven has been constructed in three different ways: With horizontal ovens, inclined ovens and vertical ovens; but all seem to agree that the horizontal type is by far the best form of construction. It costs less to construct and is better to operate. While I examined and observed the operation of the different kinds, I will only describe and give data regarding the horizontal type.

When we consider the large amount of coal carbonized in one body, we come to the great, economic advantage of the gas oven as compared with the old method of making coal gas. By the proper application of machinery, not much more labor is required to charge and recharge the gas oven of the above capacities than is needed for the retort. The construction of the oven and its appurtenances permit quite as accurate a control of carbonizing temperatures, retort pressures and all other essentials that enter into the control of the product.

In short, the gas oven brings to the industry the same great economies in labor, on account of the large units handled, as we find in the American steel plants, for instance, where 100 ton open hearth furnaces have replaced the 15 and 20-ton furnaces of earlier European practice, and in our great blast furnaces, where increased capacities permit an output of 400 to 500 tons of iron per day, with almost the same crew of men that were formerly employed to obtain a product of 400 to 500 tons of iron per day, with almost the same crew of men that were formerly employed to obtain a product of 400 to 500 tons per week.

Production of Maximum Gas with Minimum Coke.—The production of illuminating gas from by-product coke ovens has become an old story in America, since about 50,000,000 cu. ft. per day, or 14 per cent of the entire gas coal product of the country, is produced by the by-product oven. But the gas oven makes a distinct step in advance from these plants, of especial interest to gas men. Instead of consuming from 50 per cent to 60 per cent of gas made in heating the oven, the gas oven is fired with producers in essentially the same manner as the modern gas retort, and the entire product of gas from the distillation of the coal is available for sale. This makes the economies of the by-product oven available for very many gas men to whom, heretofore, the large production of coke per 1,000 of gas was an insuperable objection. Producer gas may be applied to the heating of gas ovens with quite as much economy as in the full depth retort plants, and either a portion of the coke produced or

*Paper by George F. Goodnow, presented at the eighth annual meeting of the Illinois Gas Association, Chicago, Ill., March 20 and 21, 1912.

bituminous coal may be employed as producer fuel. Moreover the quality of the coke made in the gas oven is of much higher grade and if proper coal is selected, good metallurgical coke may be produced without injury to the quality of the gas.

The gas oven permits of a wider range of coals than is possible in the retort, since it is essentially practical and economical to bring up the grade of the gas produced by taking off during the last portion of the carbonizing period the thin, blue gas that is made, especially when some of the leaner coals are used, thereby maintaining the standard of B. T. U. or of candle power at any desired point with accuracy. This lean separated gas is, of course, used as fuel for heating the ovens.

In Vienna I visited the municipal plant in which 18 large horizontal ovens were in operation, and had been in use then for 5 or 6 months. Eighteen more were under construction in this station and 72 more ovens were in the course of construction in a larger new plant on the other side of the city of Vienna. At the first named station, a block of inclined ovens, constructed by the same maker, had been in operation for a longer period, but the experience in operating these inclined ovens was not satisfactory enough to lead to the construction of more of this kind.

The engineers of the city of Vienna, evidently strongly approved of the horizontal ovens of this design, which are constructed by Heinrich Koppers, of Essen, Germany. The firm of Koppers had previously had wide experience in the construction of by-product ovens in the coke regions of Germany, and also had large installations at different points in the United States.

The battery of 18 ovens in operation, above referred to, would produce about 2,000,000 cu. ft. of gas per day. Each oven receives a charge of coke of about 11 tons. The furnaces were heated with producer gas generated in a separate plant nearby. It required 18 men for 24 hours to operate this plant, at a very low labor cost per 1,000 cu. ft. produced, but it must be borne in mind that the cost of labor in Vienna is less than $\frac{1}{2}$ that which obtains in this country. This labor ranges from 65 cts. to \$1.10 per day.

The charging and discharging are done at the rate of 5 ovens per hour. Therefore, all the work of this nature is done between the hours of 7 and 11 a. m., leaving nearly all of the men at liberty to do work of other kinds in the afternoon.

Coal used in this plant is from Silesia, containing over 11 per cent ash and 3 per cent moisture, and does not have the appearance of high grade gas coal. Still the production of gas averages 5 ft. to the pound, with a heating value of 587 B. T. U.'s to the cubic foot. This is the average result of carbonizing 1,782 tons of coal over a period of 9 days. The fuel coke used in the production of the product gas to carbonize a ton of coal is 15.7 per cent. There is no standard of illuminating value required in Vienna, the heating value

being the only standard maintained, and this is true in about all European cities.

Another design of gas oven used in many cities of Continental Europe is that constructed by the Messrs. Kloeene, of Dortmund, Germany. These ovens are smaller in coal capacity and are heated with recuperative furnaces, using coke for fuel, similar to full depth retort benches in this country. I will comment briefly on a few installations of this design which I inspected.

The first one I had the privilege of inspecting was operated by the Municipality at Padua, Italy. There are 16 ovens in this installation—each oven 19 ft. 8 ins. long, 7 ft. 10 ins. high, 14 ins. wide at the pusher end, and 16 ins. wide at the discharge end. The charge of coal was 8,800 lbs. per 24 hours for each oven and the yield of gas was given at about $5\frac{1}{2}$ cu. ft. per pound. The coal in use was imported from England. The coke used for fuel in the furnaces averaged 16 per cent, by weight, of the coal charged. The product of this plant was about 700,000 cu. ft. per day and the charging was all done during the day time, this work beginning at about 8 o'clock a. m., and during the next 2 hours half the ovens were charged. In the middle of the afternoon the other half was charged, the charging for the day being completed about 4 o'clock in the afternoon. This left the labor for the night confined to feeding the furnaces and looking after the exhausters, which required the services of only one or two men.

In the city of Rixdorf, Germany, which is practically a part of Berlin, the municipality conducts the gas plant, part of the gas being made from Kloeene ovens similar in design to those described at Padua. Each has a capacity of about 4 tons of coal for 24 hours.

I also inspected vertical settings at Dortmund, constructed by the same firm. I was informed that other work was in the course of construction in Italy, at Boulogne and Genoa, and a prospective contract in Naples.

At Versailles, near Paris, I examined another horizontal setting of about the same size as that in Padua.

At St. Gilles, near Brussels, Belgium, I was enabled to observe the operation and secure very complete data, extending over an operation of 12 days, from April 1st to April 12th, inclusive. The average results of this period were as follows:

Total gas made, 9,364,384 cu. ft. Amount of coal used to produce this amount of gas was 1,785,960 lbs., which shows an average of about 5.25 cu. ft. of gas per pound of coal. The coal was a mixture of half German and half English, with the following partial analysis:

	German coal. Per cent.	English coal. Per cent.
Ash	8	10
Water	2 to 3	2 to 3
Volatile matter.....	30	28 to 29

The average B. T. U.'s were carefully measured during three days in March and the record was as follows:

March 21, 1911.....	606
March 22, 1911.....	606
March 23, 1911.....	625

On March 23rd the heating value of calories was determined by measurement each hour of the day in calories per cubic meter. The lowest point was 8 a. m., 4,579 calories, and the highest point was at 4 p. m., 6,492 calories. The average for the 24 hours, converted into B. T. U.'s, showed 625 per cu. ft. The variation in heating value is explained by the system of charging, which was from 7 to 9 a. m. and 1 to 3 p. m. each day, and no charging was done at night, consequently the poorest gas was going into the holder at 8 o'clock in the morning.

The requirements by the municipality were not much more than 500 B. T. U.'s to the cubic foot, so that the gas from these ovens was thinned out with a lean water gas manufactured in a separate water gas plant and mixed in the holders.

This setting, consisting of 18 chambers, was constructed in an old retort house and built to fit the building. The dimensions were $16\frac{1}{2}$ ft. long by 6 ft. 3 ins. high, and 15 ins. wide at the pusher end and $17\frac{1}{2}$ ins. at the discharge end. Labor required to operate this setting was 4 or 5 men through the day time. The coke handling was very crude, and done by cheap hand labor with no particular view to economy, being a municipal plant, and it seemed necessary to employ as many men as could be conveniently used.

A plant of this design is now being built by the Central Indiana Lighting Co. at Muncie, Ind., with complete coke handling machinery of clever design which is being installed with a view to minimizing hand labor.

The paper presented to you last year by Mr. J. C. Markley discusses and describes this design of plant so fully and completely that it is unnecessary for me to more than comment in a very general way upon it, and record some average results.

In this country the Semet-Solvay Co. has been experimenting during several years on a design of gas oven, at Detroit, Mich., and it has perfected an installation which successfully handles American coals, heating the ovens with the individual producers, one producer to each oven. The coke is handled and quenched mechanically, the whole process being done with practically no hand labor.

The original designs of coke oven plants of the Semet-Solvay pattern were first constructed in the iron regions of Germany and Belgium, and have been adapted and perfected by American engineers, so that it is believed that they are superior to European construction, and are now being adapted to the production of a maximum of gas and minimum of coke.

It was finally decided to construct a small block of these ovens at Waukegan, Ill., and 13 of them are now in course of construction at that point and are expected to be in operation about July 1.

The dimensions of these ovens are 30 ft. long by about 9 ft. high, $17\frac{1}{2}$ ins. wide, at the pusher end and 19 ins. at the discharge end and will contain about 9 tons of coal each. The power to drive the pusher, conveyors, coke car, etc., will be with electric motors. The

steam for generation of electric power will be from waste heat, water tube boilers interposed into the flues of ovens. One of these boilers will be fitted for coal firing by hand in case of need.

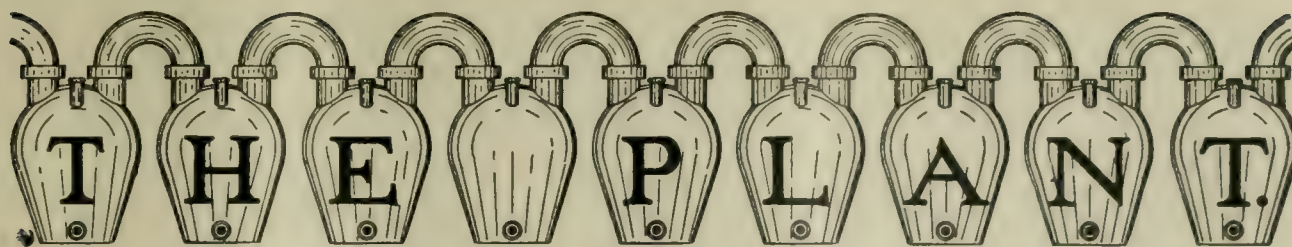
Coal will be received into a hopper delivered from coal dump cars, elevated and crushed into storage bins from which it falls into a large larry, which, in turn, dumps into the ovens. When the hot coke is pushed it will be discharged from the quenching car to the coke handling apparatus for screening, sizing and loading on cars or to the stock pile. No hand work is contemplated in the whole operation. The ammonia will be absorbed and concentrated and marketed as concentrated liquor.

It is believed that, with American coals, of high volatile contents, a good grade of gas will be made of high heating value. This plant will be located on a 10-acre lot with good transportation facilities, the coal being switched from a dock on the Waukegan harbor not far distant.

The discussion of the operation of gas ovens in this country involves more than the mere production of gas, and means the disposal of approximately 50 tons of coke to each million feet of gas produced. There is not much question that the coke can be readily disposed of for domestic purposes, to say nothing of its utility in furnace and foundry work.

While the office of a prophet is often a dangerous one, it does not appear difficult to foretell with safety the establishment of markets for tar and ammonia on a more stable basis than they have heretofore had. The uses of ammonia in the arts are multiplying and the great field of sulphate for fertilizing use is only just entered upon. The uses of tar and its products are also multiplying, the one that is just now growing rapidly is the tarring of highways. With the introduction of the automobile some elastic road binder has become almost essential to the maintenance of highways, and coal tar in one or more forms seems to meet this demand as well as any other material. As a binder for briquetting coal, which has long been an established industry of great importance on the Continent of Europe, is attracting much attention in this country and promises to be the means of bringing into the market many coals, especially in the West, which cannot otherwise be put into merchantable form. From coal tar derivatives there are many possibilities of great industries which have hardly had a commencement in this country. Germany has pointed the way and America will naturally follow as soon as we have had time to solve the new problems arising from the different conditions existing here.

There is a growing demand in Chile for sulphur to be used in the manufacture of low-grade powder so extensively employed in the nitrate works of the northern part of the country. The imports for 1910 amounted to 3,081,476 pounds, of which Italy supplied 50 per cent, Germany 41 per cent, and Japan 8 per cent.



EXTRACTS OF CELLULOSE.*

By M. LOUIS SODY.†

Origin of these extracts.—The great and ever increasing use of paper long ago rendered it necessary to find sources of raw material in addition to the rags, of all sorts, old rope, tow and old paper which had long sufficed for the manufacture of paper. Analysis having shown that the cellulose of plants is essentially similar to the material of rag papers, attention was naturally directed to the vegetable kingdom in the search for a substitute for rags.

The problem to be solved in the chemical production of wood pulp consisted in extracting from the woody tissues the cellulose which they contain, in such a condition of length, strength and elasticity that it could be felted together in the manner essential to the making of paper. There are evidently many possible ways of extracting the cellulose from wood, but a study of them is foreign to the purpose of this lecture. The system most used in the making of wood-pulp is as follows: The wood is reduced to small chips by a suitable machine, or ground in a mill, so as to expose as large a surface as practicable to the action of the chemicals. The chipped wood is placed in autoclaves or specially constructed vats, where it is treated with a solution of acid calcium sulphite ("bisulphite of lime"). The wood is thus disintegrated, the cellulose remaining undissolved in a more or less pure form, having a yellowish color. The liquid which flows away is brownish black. This liquid holds in solution the tanning matters, carbohydrates and salts.

Since no way of utilizing this liquid had been discovered, it was formerly turned into the streams, producing great pollution of the water. The nuisance to those who lived along the streams became unbearable, and a law was passed forbidding the diversion of these wastes into the streams. Being thus compelled to find means of disposing of these residues, the manufacturers sought for a market for the matter contained in them. Chemists attacked the problem, and considering the composition of the wood before being treated with bisulphite, they reasoned that the residue ought to contain tannin. We know that wood is made up of cells whose walls are of cellulose, vas-

culose and cutose cementing these cells into the vessels and fibers, which make up the organic tissues. Finally, the cavities of these cells are filled with amidon, gums, resins, and tannin, which together with mineral salts make up the chemical constitution of the plant. Since the manufacturing process separates the cellulose from all the other materials, a considerable amount of tannin ought to be found in these residues. They cannot be used directly to make leather, not only on account of their dilution, but also because of the presence of too great proportions of lime and of bisulphite. Such a tanning material would make brittle leather. The presence of these substances is not, however, an insurmountable obstacle to the use of these wastes in the tannery; special processes have been devised to neutralize the injurious effect of these various substances. After this treatment the liquor is concentrated, and a new tanning material takes its place among the many products offered to the tanner.

This new substance, so-called tanning material, was introduced successively into England, Germany and Austria. It appeared in Belgian markets two or three years ago, but has not as yet come into extensive use.

Is the pulp extract a tannin?—What is the chemical constitution of this product, and can we consider it a tannin? The chemical nature of tannin is not well understood, so that in order that a substance may be considered a tannin we say that it must respond to certain tests. It must, first, have an astringent taste and a feebly acid reaction; second, it must precipitate the alkaloids and gelatine from their solutions; third, it must precipitate certain metallic salts, such as ferric chloride, and with this it must make a black, green or blue coloration; fourth, it must combine with alkalis to form products which blacken when oxidized by exposure to the air; fifth, it must unite with skin tissues to form an imputrescible substance called leather; sixth, it must dissolve in water, alcohol and acetone and be insoluble in chloroform, carbon disulphide and ether.

Cellulose extracts do not fulfill all of these conditions. That is why they are not considered to be tannin in the same sense as quebracho, chestnut, oak and mimosa. This substance is not a tannin extract, but is, as we have seen from considering its mode of manufacture, a concentrated solution of vegetable matters from the substance of the wood, containing certain colloidal substances absorbable by hide powder, as are certain other non-tannins, such as gallic acid.

There are on the market different kinds of cellulose extracts of varying degrees of concentration, and

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differing in the proportion of tannin to nontans. The nontans include many substances both mineral and organic. The percentage of mineral matters may be as high as 9 per cent, including salts of lime, of magnesia, of manganese, and even of iron and alumina. The organic nontans are largely carbohydrates, and of these the most part are reducing sugars, since the amount of Fehling's solution reduced is not increased by acidification.

Analysis of these extracts by Proctor's filter-bell method indicates a tannin content from 20 to 30 per cent, and nontans from 20 to 37 per cent. But the filter-bell method is not a scientific method; it shows the matters absorbable by hide powder, while the scientific method of Löwenthal is based on the oxidation of the tannin by permanganate. This method gives a tannin figure for cellulose extracts about one-sixth as great as the filter-bell method. This difference in results is explained by the fact that the potassium permanganate indicates with considerable accuracy the quantity of gallo-tannic acid present. The quantity of gallo-tannic acid in the cellulose extract is therefore only that shown by its reducing effect on the permanganate.

M. Lepetit has found a term well adapted to this sort of extracts. He calls them pseudo-tannins. The cheapness of these extracts is an invitation to fraud and they are found mixed with other extracts in the market, mainly chestnut. The hide powder method does not show its presence, but the permanganate method has cooled the enthusiasm of the adulterators. This method not only shows the presence of cellulose extract, but even permits the amount added to be estimated.

Proctor has worked out a method for detecting the presence of sulphite-cellulose in extracts. Since aniline is the test for ligneous materials, the presence of this substance may be detected in the following manner:—To 5 cc. of a tannin solution, add one-half cc. of aniline; shake; add to the mixture 2 cc. concentrated hydrochloric acid. This addition of acid immediately clears up the slight cloudiness caused by the aniline, giving a clear solution whenever cellulose extract is absent. If such extract be present, an abundant precipitate forms, which gradually rises to the surface. If this test causes a slight cloudiness only, the presence of cellulose extract is not proved since such a result may be due to faults of manufacture in an extract which has not been sophisticated.

Other methods of detecting cellulose extract might be mentioned, but of all the means tried at the Liège Tanning School, none has given results so satisfactory as the titration with potassium permanganate and the phenylamine test. We have mixed quebracho extract with cellulose extract and percentages of tannin as shown in the following table were obtained, using

the hide-powder (shake) method and the method of Löwenthal:

Quebracho per cent.	Cellulose per cent.	Tannin	
		Hide-powder.	Löwenthal.
Pure	—	36.0	35.3
20	80	32.8	10.2
40	60	33.5	16.4
60	40	34.1	23.4
80	20	35.3	29.3

Finally, Yocum and Faust, in an article published in the Journal of the American Leather Chemists' Association (VI, 537), make an interesting observation: When sulphite cellulose extract is mixed with a tanning extract, loss of tannin takes place, and this loss is greater where the proportion of sulphite-cellulose extract is greater. Exceptions are noted in the case of sulphited liquid quebracho, and in one or two other instances where the proportion of sulphite-cellulose was only 10 per cent. A mixture of equal parts of cellulose extract and chestnut showed a loss of 6 per cent, a similar mixture with myrobalans from 3 to 4 per cent and valonia nearly as much. Another American chemist, Mr. H. C. Reed, has offered an explanation of these facts: Hide powder placed in contact with a mixture of cellulose and chestnut extracts, absorbs first the tannin of the chestnut, and being then partially tanned has less power to absorb the cellulose extract than untanned hide powder. This explanation assumes that hide has not so great an absorptive power for cellulose extract as for the other tannins. In a mixture of cellulose extract and sulphited quebracho, such action was observed, but in a much smaller proportion. Some mixtures were analyzed with the following results:

Tannin found per cent.	Theoretical tannin per cent.	Non-tan found per cent.	Theoretical non-tan per cent.
10.3	11.47	6.3	5.18
8.24	8.92	8.3	7.56
5.82	6.35	10.64	9.94

We have performed about a score of analyses of mixtures, and in every case have found less than the theoretical amount of tannin, and therefore higher nontans.

Use in the tannery.—I have reviewed the history of cellulose extracts, and indicated their special characteristics: the most important question remains to be discussed. What is the value of cellulose extracts in the tannery, and can they be employed with success? Aided by Messrs. C. Hendricks and René Lefebvre, I have made some experiments in tannage at the Liège Tanning School. I wish to thank my two collaborators and to say that if my work yields results of value, a good share of the credit is theirs.

A strip of hide as uniform as possible in thickness and condition was cut into pieces of similar size and as nearly as possible of the same weight. The different samples varied in thickness from 3.3 to 3.5 mm. After being well washed they were placed in a 0.25 per cent solution of boric acid for 24 hours. Boric acid was chosen as the plumping agent because of its

moderate action.¹ The thickness of the samples after treatment with boric acid varied from 3.5 to 3.8 mm., and their weights from 40 to 45 grams. We then tanned the pieces in liquors made up and analyzed in advance, as follows (Table I):

TABLE I.

No.	Composition.	Density Baumé	Total extract per ct.	Tannin per cent.	Non- tans per ct.
1	100% quebracho.....	8.8 at 16° C.	16.30	14.57	1.73
2	75% quebracho..... (25% cellulose)	9.5 at 16° C.	16.46	10.30	5.5
3	50% quebracho..... (50% cellulose)	9.4 at 16° C.	16.54	8.24	8.3
4	25% quebracho..... (75% cellulose)	8.8 at 16° C.	15.80	5.82	10.64
5	 (100% cellulose)	9.5 at 16° C.	16.00	3.68	12.32

A rapid method of analysis was used, that is to say instead of chroming the hide powder, washing it, etc., we mixed a known weight of hide powder with the tanning solutions to be tested. Corrections were necessary on account of soluble matter in the hide, etc.

The samples of hide with their liquors were placed in bottles and stood for some hours. The rotary shaker was then started, and after 29 hours of rotation the samples were examined. They seemed to be completely tanned. They were, however, shaken 10 hours longer, then washed, and after soaking in pure water for 15 minutes, weighed. The rendement, for 100 parts white weight was as follows:—The leather tanned in liquor No. 1, 119.5 per cent; No. 2, 109.5 per cent; No. 3, 106.5 per cent; No. 4, 117.5 per cent; No. 5, 116.5 per cent.

The appearance of the samples varied considerably. That tanned in pure quebracho was red, and firm to the touch; that from liquor No. 2 was brownish and fairly firm; that from No. 3, dirty gray, supple and soft; that from No. 4, grayish and very soft; that tanned in pure cellulose extract very soft and light yellow. In order to estimate the tannage, cuts were made in the samples, and they were found to be completely tanned. The pieces were smoothed, lightly oiled on the grain to prevent oxidation, and suitably dried. The spent liquors were analyzed, with the following results:

No.	Density Baumé	Total extract per cent.	Tannin per cent.	Non-tans per cent.
1	7.0 at 21° C.	12.29	11.13	1.16
2	6.9	12.11	7.22	4.88
3	7.4	13.06	5.62	7.44
4	8.0	13.07	3.94	9.76
5	8.3 at 19° C.	14.12	2.48	11.64

Comparing the new and spent liquors we find a tannin absorption varying according to the proportions of cellulose extract employed. The tannin absorbed from liquor No. 1 was 3.44 per cent; from No. 2, 3.08 per cent; from No. 3, 2.68 per cent; from No. 4, 1.88 per cent and from No. 5, 1.20 per cent. After drying, the pieces were again examined, and here a surprise greeted us. While all the pieces had before drying seemed perfectly tanned, it was now seen that only the sample tanned with pure quebracho was really tanned. The others showed a distinct line in the middle, which was more pronounced in propor-

tion as the proportion of cellulose extract was higher.

The rendements of finished leather based on 100 parts white weight were: No. 1, 66.3 per cent; No. 2, 61.7 per cent; No. 3, 59.4 per cent; No. 4, 57.5 per cent; No. 5, 53.8 per cent. These results scarcely need explanation. A glance at the table sufficiently indicates the action of cellulose extract on tannage. This result is scarcely surprising, after the studies undertaken by various chemists, especially the work of Parker and Blockley recently published in *Collegium* on the value of nontans in tannage. It had been previously supposed that nontans easily penetrated the fibers of the leather and gave a higher rendement. It had also been said that particularly in drum tannage a high percentage of nontans had a good influence. These gentlemen have shown that up to a certain point the nontans in an extract may penetrate the fibers and give weight to the leather. They conclude from their experiments that a high proportion of nontans does not tend to make either firmer or heavier leather. This study was very interesting, and bears upon the subject we are discussing, for we found that in proportion as the nontans were increased by addition of cellulose extract, the rendement decreased. I believe that cellulose extract employed in mixtures with other extracts is an obstacle to tannage in a drum. In vat-tannage this extract may give rise to the acids necessary to the plumping of the hides, but may through the weakening of the liquors, diminish the rendement.

We wish to verify the rendements by analyzing the pieces of leather, thus learning the proportions of hide and of combined matter in each. The nitrogen was determined by the Kjeldahl method. This method enables us to follow tannage through its various phases. The proportion of hide diminishes as tanning proceeds, and the combined tannin increases until the hide has taken up all the tannin with which it can combine.

The following results are from the dried and extracted leather: Percentage of hide-substance in No. 1, 58.57; No. 2, 64.13; No. 3, 67.17; No. 4, 67.30; No. 5, 74.35. On an air-dry basis, these give the following figures:

Number.	Hide substance per cent.	Combined tannin per cent.
1	43.30	30.58
2	46.25	28.29
3	49.57	24.23
4	49.02	23.82
5	51.39	17.73

One may ask after this study, of what value cellulose extract is. We have placed a piece of quebracho tanned leather in a solution of cellulose extract of 9° Bé, for some hours, with agitation. The leather so obtained was treated in the same manner as the other pieces, dried and weighed. The rendement was raised from 66.3 per cent to 70.9 per cent by the retannage. This leather was analyzed to find out whether a part of the tannin of the cellulose extract had been fixed upon the hide. But on washing in water the materials which had raised the rendement were nearly all

¹Wood, Hough and others say that boric acid has no plumping effect.—Editor.

washed out. Cellulose extract may be used for retannage of leather in place of such other extracts as cutch and gambier, and may advantageously replace glucose and molasses. Besides this value as a retanning agent, cellulose extract has another advantage which is peculiar to itself; it acts as a decolorizer. Quebracho, mangrove and divi-divi leathers have a very disagreeable brown color. Cellulose extract corrects this color most satisfactorily. A solution having 75 per cent quebracho and 25 per cent cellulose gave a leather of a light rose-color; equal parts gave light brown and 25 per cent quebracho and 75 per cent cellulose gave light yellow. Pure cellulose extract gave a yellow leather which shrivelled in drying. Leather tanned with quebracho having a disagreeable red color is changed to a color similar to that of oak leather by retannage with cellulose extract.

An equally interesting point is in regard to the drying of leathers tanned with mixtures of cellulose extracts, especially retanned leathers. It is well known that light has an influence on the color of some tannages. Youl and Griffith made experiments to determine the actual effect. They found that the tannages least affected were those of oak-wood extract, chestnut extract and valonia, while leathers tanned with quebracho, mimosa and hemlock were much darkened. We found that when a part of one of our pieces tanned with mixtures of cellulose extracts was exposed to the light while drying, the part exposed was much darker in color. It is therefore important not to expose retanned leather to the light while drying.

NEW GERMAN ALUMINUM GALVANIZING PROCESS.

In a new process for galvanizing aluminum patented in Germany, the previously cleansed aluminum is scoured in the ordinary manner and then dipped into a heated acid solution and simultaneously subjected to the action of reducing agents, such as alcohol, which prevent a too rapid reaction. After being in this solution for a brief time the aluminum is transferred to an ordinary galvanizing bath. According to experiments, galvanizing thus executed is both durable and can be given a remarkable polish. As we know, application by electrolysis of a coat of metal on aluminum has hitherto been difficult, and now the "Langbein-Pfanhauser Werke," of Leipzig-Lellerhausen, claims to have invented a process, after much study and experimenting, which gives the required result, states *The Metal Industry*. In this process the metallic coat deposited on aluminum plates is absolutely adhesive. Articles made of galvanized aluminum were bent in all directions, heated to a high temperature in a flame, and suddenly chilled in cold water, without the coating being broken. More than this, these same objects were bent to breaking point without the deposit of metal being detached. Aluminum can thus be plated with gold, silver, brass, copper or nickel.

THE PRODUCTION OF ETHYL ALCOHOL FROM WASTE PRODUCTS.*

The first synthesis of ethyl alcohol was made about 1826, by Hennel, utilizing the reaction of ethylene and sulphuric acid to form sulphovinic acid which, upon heating with an additional quantity of sulphuric acid, yields alcohol. Berthelot improved this process by synthesizing ethylene from its elements via acetylene, and by making a more complete conversion of ethylene into sulphovinic acid.

The one source of the alcohol is the action of the zymase of yeast upon glucose and other fermentable sugars. The sources of the fermentable sugars may be grouped into two classes:

(1) The products of the hydrolysis of starch and allied substances by means of an amylase.

(2) Solutions of sugars obtained directly from fruits and plants and from the non-crystallizable by-products of sugar-works—such as molasses.

The most economical source of starch in our country is probably Indian corn costing about \$21.00 per ton. One ton of corn gives about ninety gallons of 94 per cent alcohol. About two gallons of raw molasses produce one gallon of 94 per cent alcohol, and this raw material costs about \$0.21 per gallon of 94 per cent alcohol. The costs of the distillation of the mash and the rectification and purification of alcohol cannot be entered into here, but the approximate cost of 95 per cent alcohol (190 proof) to the consumer may be taken as about 50 cents per gallon, exclusive of taxation.

Within the last two or three years, two new commercial processes for the production of alcohol have been put in operation on a comparatively large scale. The purpose of this article is to present and discuss briefly from a chemical engineering standpoint these two processes; namely, the production of alcohol from sulphite cellulose waste lyes, and the production of alcohol from sawdust.

I. ALCOHOL FROM SULPHITE LYES.

In the sulphite process for the production of pulp, for every ton of cellulose there are about ten tons of sulphite lyes (T. H. Norton, U. S. Cons. Rep., Nov., 1911), which contain one-half the weight of the wood originally introduced into the boilers. Among the substances present are: dextrose and other sugars, xylose, acetic acid, tannic acid, nitrogen compounds, methyl alcohol, resins, etc., and calcium lignin-sulfonate, the chief product of the reaction. Most of the sugars in these lyes are fermentable and they constitute about 1 per cent of the lyes, the yield of alcohol being from fifteen to seventeen and one-half gallons per ton of cellulose [C. G. Schwalbe, Z. angew. Chem., 23, 1537 (1910)].

Recently in Sweden two industrial processes have been developed, that of Ekström (P. G. Ekström, Eng. Pat. 6741, March 17, 1910) at Skutskar and that

*From the Journal of Industrial and Engineering Chemistry.

of Wallin at Forss. These processes are practically identical, differing only in the neutralization of the acid. The former uses lime, chalk, etc., and the latter waste causticization sludge. The general scheme is as follows: The lyes are first neutralized in large vats, then cooled in towers and aerated. In a mill producing ten tons of cellulose per twenty-four hours the volume of the lyes to be treated is about nine thousand gallons per day. A yeast nutrient, malt extract or dead yeast is added to the cool, neutral liquid which is transferred to the fermentation vats. After fermentation (which takes three days or more) the yeast is separated and the liquid distilled in a continuous still. The percentage of alcohol is very low and considerably more steam is used in the distillation than is required with mash from molasses which usually contains about 7 per cent alcohol by volume. The alcohol obtained is already denatured as it contains considerable methyl alcohol (from the unfermented lyes), furfural, aldehydes, and sometimes acetone, but is practically free from terpenes.

The above process with a few minor changes is being worked on a large scale at several places in Sweden. The experimental plant at Skutskar began operations on May 24, 1909, using waste lyes from a 5,000-ton cellulose plant. In March, 1910, 560 gallons of "normal strength" alcohol were produced per 24 hours. The total for the month was about 13,000 gallons. The process yields about 6 gallons of absolute alcohol for 1,000 gallons lye, and about 14 gallons for every ton of cellulose.

As the alcohol produced from waste lyes is denatured, its chief uses will necessarily be for heating and other industrial purposes. The industrial prospects of this process depend on the cost of production, conditions of taxation and capacity of the market. Estimates of the cost of production for a mill producing 340,000 gallons per annum place the cost at about \$9.50 per 100 gallons. In Sweden the tax per gallon increases with the output, so that for an annual production of 340,000 gallons, the cost of production including the tax is about \$15.50 per 100 gallons. In Germany excise regulations penalize new distilleries so that in addition to the cost of production, sulphite spirit would be subject to a tax of about \$17.00 per 100 gallons. Regarding the capacity of the market, in Sweden during the fiscal year 1908-1909, the total production of alcohol was about 5,800,000 gallons (absolute) and the imports were about 310,000 gallons. The sulphite lye mill at Larkudden is reported as having produced spirit during the year 1910 at the rate of 157,000 gallons per annum, and the annual rate of production at the present time is estimated at 250,000-400,000 gallons. The pulp mills of Sweden can produce 6,500,000 gallons of absolute alcohol per annum. It must be remembered that the present method of production from grain is always intimately connected with the agricultural industries of the country, and therefore will not be easily displaced. Also, while under special conditions (espe-

cially low taxation) the sulphite process can be worked at a profit, yet it does not solve the problem of the disposal of the waste lyes, as only about 1 per cent of the total weight of lyes is converted into alcohol. In fact on account of the presence of dead yeast, etc., the problem of the disposal of the lyes may be aggravated by the use of this process.

II. ALCOHOL FROM SAWDUST.

The cost of raw material is always of great importance in any industry. While Indian corn costs about \$21.00 per ton, sawdust in the vicinity of a large mill where it is a by-product can be bought at a cost of 30-50 cents a ton including handling and transportation (short distances). One ton of sawdust calculated to the dry basis can yield 20 gallons of 94 per cent alcohol, which makes the cost of this raw material 2-2½ cents per gallon 94 per cent alcohol, as against 24 cents for Indian corn.

For nearly one hundred years it has been known to chemists that fermentable sugars can be produced from sawdust. The reaction is usually spoken of as being very simple, all that is necessary being to add a molecule of water to the cellulose. This hydrolysis is probably as complex as it is baffling. The unknown composition of those polysaccharides which we call cellulose and the very different results obtained on hydrolysis under slightly different conditions of catalyzer, temperature and pressure indicate that somewhat intricate reactions occur, the complete chemistry of which is not known at the present time. A very large number of patents have been granted on this reaction, the main differences being in method of manipulation and the catalyzing acid used. Sulphuric acid has been used in many cases but the subsequent removal of this acid has proved a serious stumbling-block. No process that was capable of commercial application had been devised until the year 1900 when Dr. Alexander Classen was granted his first patent. The more important English patents granted him are: No. 258, Jan. 4, 1900; No. 4,199, Feb. 27, 1901; No. 12,588, June 20, 1901. "Process claimed consists in boiling cellulose in a closed vessel at a temperature of 120-145° C. with a solution containing sulphurous and sulphuric acids or sulphurous and hydrochloric acids. A solution of 2 per cent or more of sulphurous acid and 0.2 per cent sulphuric acid is mentioned. The sulphuric acid may be conveniently formed in the boiler by admission of air or other suitable oxidizing agent. In this way concentrations of 10 per cent sugar may be obtained, 80-90 per cent of which is fermentable. Conversion is complete in 15 minutes."

An experimental plant using this process was erected at Aachen and a similar plant on a larger scale was built at Highland Park near Chicago. The results were satisfactory so that it was decided to build a commercial scale plant at Hattiesburg, Miss. The capacity of the conversion cylinder was two tons. After the conversion the acid was neutralized, cleared by subsidence, pumped into large vats and fermented

by yeast and then distilled. From a commercial viewpoint this plant was a complete failure. From a chemical engineering standpoint it is an excellent example of a process which fell just short of success. The reasons given for the failure are: (1) Length of time required for conversion: $1\frac{1}{2}$ -2 tons requiring 4-6 hours. (2) Prolonged action produces gums and caramels and makes extraction of the sugar tedious and expensive. (3) Large quantity of acid required. (4) Lining difficulties, especially with lead linings.

Two chemical engineers, Ewen and Tomlinson, studied and undertook to improve this process. Their patent U. S. 938,308, 1909, describes their process. The converter used by Classen was about thirty feet in length and had a diameter of three feet, whereas in the Ewen and Tomlinson process the digester is much shorter, usually being about twelve feet in length and eight feet in diameter. The latter line their converter with fire-brick instead of using the troublesome lead lining. The operation seems to be fairly simple. Sulphur dioxide gas to the extent of 1 per cent of the weight of the wood is introduced into the cylinder and live steam is turned on until a pressure of 100 lbs. is obtained. The steam is then turned off and the cylinder slowly revolved for 40-45 minutes, the temperature and pressure being kept constant. The total time of conversion is about one hour as against 4-6 hours in the old process. In operating this process it is important to raise the temperature as quickly as possible to the "critical point" which is defined as "that temperature above which the production of unfermentable substances and the destruction of the sugars become excessive and lies between 135° and 163° C." After extraction, the converted lyes have a total acidity of 0.64 per cent (calculated to H_2SO_4) containing sulphuric, acetic acids, a small amount of sulphurous acid and aromatic compounds of the type of pyrogallol. These liquors contain about $5\frac{1}{2}$ per cent of reducible sugars calculated to dextrose. Polyphenols, tannin and furfural are usual present in small amounts. These liquors are fermented and distilled in the usual manner, some care being required in the fermentation to have present a proper food for the yeast. The distilled alcohol obtained is potable, free from the odor and taste of wood, and from methyl alcohol and fusel oils, but contains traces of furfural and aldehydes. One and one-half tons of dry wood give about $61\frac{1}{2}$ gallons of 94 per cent alcohol. From figures obtainable it appears that the efficiency of the process is from 75-80 per cent of the theoretical yield of alcohol.

The Dupont Powder Company is operating a plant at Georgetown, South Carolina, for the production of alcohol from waste woods. This plant is licensed under the Ewen and Tomlinson patents, and while no figures were obtainable, it is stated that experiments so far indicate the ultimate success of the process.

W. P. Cohoe is the inventor of a process for making fermentable glucose-like substances from cellulose and ligneous materials (U. S. Patents 985,725, 985,726, 1911). The conversion is done in two stages: first, steam is used producing acetic acid which is collected, and then steam and HCl vapors are introduced into the converter. The raw material used is generally sawdust.

The cost of production of alcohol by the sawdust process (Ruttan, *J. Soc. Chem. Ind.*, 1909, p. 1290) is said to be about equal to that of grain, although there is such an enormous difference between the cost of the raw materials. One company, however, claims to be able to manufacture alcohol by the sawdust process at a cost of 7 cents per gallon.

Without going into the details of the chemistry involved, it is striking that, although the patents claim a conversion of cellulose into sugar, the so-called true fibrous cellulose, absorbent cotton, does not yield to this treatment. Also the material left after treatment contains cellulose which upon re-treatment yields but traces of fermentable sugar. Although authorities differ, it is claimed by some that the acid acts as a catalyzer hydrolyzing the lignone complex and a proportion of the "easily attacked cellulose." The oxycellulose and the "true cellulose" are said not to be seriously altered chemically.

It would seem that there is a possibility that a process might be evolved where the alcohol conversion of the wood pulp might be made first, and then the residue subsequently utilized for the production of paper pulp.

The U. S. Consul at Madras, India, states that the annual reports of three South Indian concerns—the Travancore, Orkaden River, and Paloor rubber companies, which are all under the same management—show that these interests had the following acreages planted with Para rubber; Travancore, 1,038.78; Orkaden River, 734.3; Paloor, 399. The Travancore Rubber Co. harvested 29,600 lbs. of rubber last year; the Orkaden River Co., 4,465 lbs.; and the Paloor, nil. The estimates for this year are: Travancore, 67,000 pounds; Orkaden River, 10,000 lbs.; Paloor, 6,000 to 7,000 lbs. Particulars of the crops of the Stagbrook Rubber & Tea Estates, which have 1,022 acres in rubber and 825 acres in tea, give the following rubber output: In 1910, 10,501 lbs.; 1911, 30,000 lbs.; 1912 (estimated), 62,000 lbs. The Rani Rubber Co. (Ltd.), harvested 193,750 lbs. of rubber last year as compared with 41,983 lbs. in 1910; the estimate for the current year is 325,000 lbs. of rubber. The company harvested 14,728 lbs. in April as compared with 4,475 lbs. in April, 1911; and the total for the first four months of this year is 25,110 lbs. in contrast to 4,629 lbs. in the same period in 1911. This organization has 3,054 acres planted with Para rubber.

METALLURGY.

THE PARKS ELECTRO-CYANIDE PROCESS.*

By JOHN R. PARKS.

Heretofore, practically all successful metallurgical processes in which cyanide salts have been used to extract gold and silver from their ores have contemplated:

1. Removal of coarse particles of the precious metals by amalgamation in a separate device before the ore is submitted to cyanide attack.

2. Presentation of the more or less finely crushed ore to chemical attack by an aqueous solution of cyanide salt, to which is added an alkali to neutralize acid radicals of the ore, to save cyanide salt; this solution must also contain oxygen, either the normal amount that water will dissolve from the atmosphere, or a superabundant amount added by aero-agitating devices.

3. Separation in a clear state, by settling and filtering devices, of the aqueous solution containing gold and silver cyanides, unused cyanide salt, and complex impurities, cyanates, sulphocyanates, etc., of the base metals.

4. Continued and perfect contact of the cyanide solution with the shavings or dust of an inexpensive base metal which precipitates part or all of the precious metals.

5. Separation of the precipitated precious metals from the remaining base metal, washing, collecting, drying and compressing the finely divided precious metals for melting and casting into bullion.

The object of the Parks electro-cyanide process is to apply economically all of the chemical and physical forces necessary to extract and collect the precious metals, applying them at their highest potency, and simultaneously. This necessitates economy in chemicals, their almost instant presentation under their best operating conditions to every particle of precious metal in the ore, and for only such length of time as is required for a thorough chemical interchange. That this has been accomplished will be shown by quoting results of its application to simple and to refractory ores; all of these ores, in their raw state, were made to yield their precious metals rapidly in the form of amalgam, in a single operation, in a single machine, eliminating all filtering and precipitating devices.

The Parks electro-cyanide pan consists of a wooden tub, 15 ft. diameter and 30 in. deep, through the center of which projects a small conical casting for the passage of the working shafts. Practically the entire bottom of the pan is covered by an amalgamated copper plate, to which quicksilver is automatically added

during operation, in proportion to the amount of precious metal in the ore being treated. About 9 in. above the copper, or cathode, plate, a cast-iron anode plate equal in area to the copper plate is mechanically suspended. The cast-iron plate is divided into two annular rings, the outer one containing 60, and the inner one 40 per cent of the anode area.

These annular anodes are revolved in the same direction, and independently, by means of pulleys, gears, and a solid and a hollow shaft, so that any midway point of the inner ring travels practically the same number of feet per minute as any midway point of the outer ring. On the lower side of each of the anode rings, wooden paddles 7 in. deep are fastened radially, about 5 ft. apart, the bottom of the paddles being 2 in. above the copper plate.

The compound rotary motions of the anode rings and their paddles give to the pulp confined between them and the cathode plate a very uniform spiral motion outward, keeping the ore in a perfect state of suspension, and at a little higher speed than pulp travels down a stamp-battery plate. By the centrifugal force of the paddles, the pulp on reaching the staves of the pan is forced up between them and the outer edge of the outer anode to a height of about 16 in. above the anode, retaining the rotary motion imparted by the paddles and now endeavoring, by gravity, to seek the lower level at the center of the pan; the resultant motion is a downward and inward spiral until the ore passes over the inner edge of the inner anode, near the center cone, when it again meets the paddles and starts to repeat its cycle of travel.

At the periphery of the pan, and on a level with the cathode plate, 20 jets of compressed air are admitted through needle valves set at regular intervals around the pan. The air pressure—about 12½ lbs. per sq. in.—is sufficient to overcome the centrifugal force of the pulp against the valve exits and to keep them clear. The amount of air is calculated from the oxygen demanded by Elsner's formula for dissolving the precious metals by cyanide salt, with an allowance for unavoidable waste in mixing. The air, on leaving the valve, travels against the outward spiral motion of the pulp between the anode and cathode plates, and nearly all the excess makes its appearance as a slight effervescence around the center cone, being thoroughly incorporated with the pulp; comparatively little escapes by rising to the surface without passing between the plates. At 100-lb. pressure, 1½ ft. of air per min. is an ample supply for the pan during treatment.

The writer, during the past eight years, has experimented with many iodine, bromine and other chem-

*From the School of Mines Quarterly.

icals, seeking economy and efficiency, and has found nothing so effective and economical as commercial potassium or sodium cyanide, or the commercial double salt, together with common lime and common salt, aided by the sodium amalgam and caustic soda generated by the process.

The electrical factor of the process, which consumes from 75 to 80 per cent of all the physical power necessary to operate it, and accounts for the speed, efficiency and economy of this as compared with other processes, is worthy of considerable attention.

From a 10 to 12-volt, 400-ampere, D. C. generator, the positive wire, after leaving the switch and indicator board, is led to the mechanical portion of the pan in four branches, each of which terminates in a suitable brush; two play against the copper collecting ring on the solid shaft which drives the outer annulus of the anode, and two against a similar ring on the hollow shaft which drives the inner annulus of the anode. By this means, the electric current passes up the vertical driving shafts, insulated from the cone through which they pass, and proceeds down the driving arms and supporting rods to the anode annuli, where it is uniformly distributed.

The negative wire from the electric generator, after passing through the switch and indicator board, also terminates in four branches, each of which connects with a copper tail piece projecting through the pan, each tail being a portion of one of the four segments of the copper plate forming the cathode. Owing to the insulation of the machine, all the electric current must pass from anode to cathode through the pulp.

In treating a charge consisting of $7\frac{1}{2}$ tons of ore (dry weight) with an equal weight of water, and containing its quota of lime previously added during the crushing of the ore, such an amount of strong cyanide solution is added as to equal 1 lb. of cyanide salt per ton of ore in the pan. The correct weight of cyanide per ton of ore may be previously determined by titrating filtered samples from the pan charge during a test run for cyanide consumption. After addition of the cyanide, finely crushed common salt is added until the ammeter registers 300 to 500 amperes, at 9.5 to 10 volts, as determined by a test run. The pan is then put in motion, the air is turned on, and the quick-silver is put into its distributor.

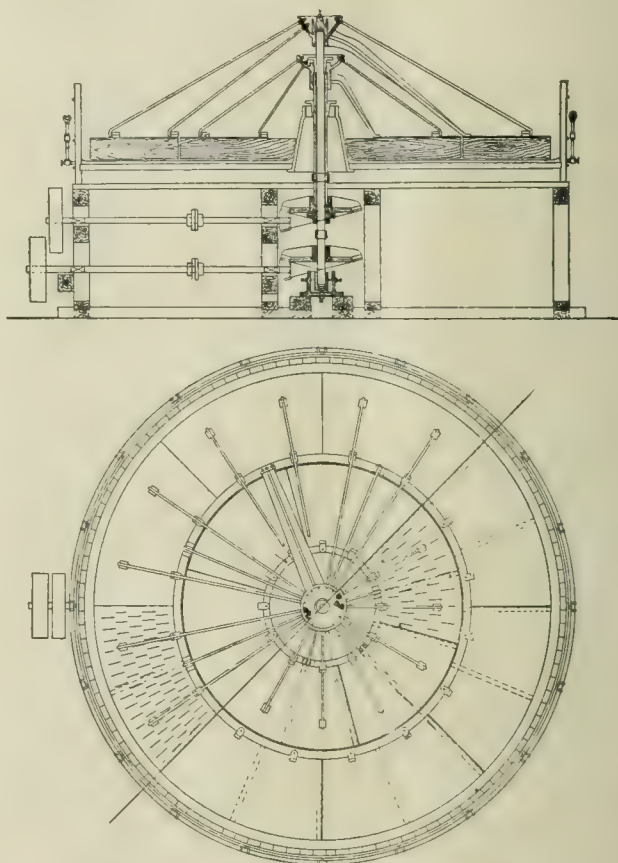
Many complex chemical compounds are formed, some of which are decomposed, in a manner which baffles the skill of the electro-chemist to explain, but among the established effects of the electric current the following may be stated:

The salt is decomposed by the electric current and metallic sodium is constantly precipitated on the mercury-coated copper plate, forming sodium amalgam; the sodium is converted into caustic soda, by its reaction with water, which, uniting with acid radicals in the ore, protects the cyanide from compounds from which the lime does not so readily protect it, thus saving a much larger portion of cyanide salt than can

be saved without the current. Chlorine is also generated, but rarely indicates its presence, probably being united with basic radicals of the complex charge.

These several ions travel very slowly in quiet solutions, but in this mechanical device the pulp travels an average of seven miles over the copper plate in a $2\frac{1}{2}$ -hour treatment, presenting the cathions rapidly for discharge and deposition. This is analagous to the method by which copper is precipitated on a platinum dish, in modern electro-analysis for copper, by a revolving anode in a small fraction of the time required for precipitation in quiet solutions.

The cyanide anion probably seizes a potash or soda radical and is reconverted into nascent cyanide salt,



Arrangement of Parks Electro-Cyanide Pan.

unless a particle of precious metal, for which it has a greater affinity, presents itself first. However, there can be no question as to the so-called restoration of cyanide, for the writer has frequently found much more free cyanide of potash or soda in a sample of solution taken a half hour or an hour after a previous sample.

Theoretically no mercury can be lost by scouring or flouring in the charge, as any subdivided particle of this metal too small to seek the cathode by gravity is sufficiently small to yield to electro-cyanide solution, whereby it is electro-chemically precipitated back on the plate. Practically, a small amount is lost, for in a 2,500-ton run on Ruth ore a loss of about 5 lbs. was reported.

On samples containing 0.8575 oz. of gold per ton, the writer has reduced the average tailing sample to

0.0075 oz. per ton, showing an extraction of 99.1 per cent by six hours' treatment in the electric pan, using 1 lb. KCN per ton of ore; the same ore, reduced to the same fineness, yielded but 92 per cent to solution in 48 hours' treatment in Pachuca tank (generally recognized as one of the best aero-agitating devices) using three tons of solution containing 3 lbs. KCN per ton, or 9 lbs. of cyanide salt per ton of ore.

Many of our western precious-metal ores from oxidized zones are contaminated by carbonates of lead, zinc and copper, which preclude economic treatment by the ordinary cyanide methods, owing to the difficulty in precipitating the precious metals in the presence of the cyanides of the base metals, aside from the excessive consumption of cyanide salt. The electric current, however, precipitates the base metals as well as the precious metals, on the amalgamated plate. The writer has produced, by the electric pan, bars of bullion worth \$1,200 or \$1,400 which averaged but 512 fine in precious metals, the other 50 per cent of the bars being lead, zinc and copper, alloyed with the precious metals. The refining charges on such bullion are low.

As precipitation of precious metals takes place more rapidly from strong than from weak solution, in treating certain ores economy can be introduced by discharging the pan at a fixed value of unprecipitated precious metals in solution (50 c. to \$1 per ton). After passing the charge through a revolving settler used as a precautionary amalgam trap, it may then be sent through a Dorr thickener, whereby 50 per cent of the solution from a 1:1 charge, and 80 per cent of that from a 1½:1 charge, can be returned clear for original charges; this not only saves time and increases the daily capacity of the plant, but secures a higher percentage of recovery of the precious metals, while preventing undue waste of common salt and unused cyanide.

The total horse-power required for a single pan is 0.6 h.p. for mechanical agitation; 1 to 1.5 h.p. for compressed air; and 4.5 to 6 h.p. for electric current.

The capacity of the pan depends on the amount and character of gangue in the ore and on the nature of its precious metal minerals. The proportion of gangue determines whether one ton of ore may be treated with 1 ton or will require 1½ tons of water; none but the very clayey types require the 1:1½ charge.

A single pan charge of the 1:1 class is 7.5 tons of ore, dry weight, and of 1:1½ ore, is 6 tons; the time required for treatment varies from 1 to 12 hours, generally being 2½ to 4 hours; hence the capacity of the pan, allowing for charging and discharging, varies between limits of 15 to 90 tons per diem, but on the average run of ores it varies from 36 to 60 tons per diem.

The large capacity of the pan, the small tonnage of ore under treatment in the mill at one time, and the small amount of machinery and apparatus required,

reduce the total cost of installing mills using this process to 30 to 60 per cent of the amount necessary to install any other process of equal daily capacity.

A few examples will show the efficiency of the process.

Ruth Gold Mining Company's mill, Kingman, Arizona.—Daily capacity 50 tons. Quartz ore with large amount of manganese minerals; little free gold. Values occur in sulphide minerals; ratio of gold to silver 1 to 12. Test in 40-in. testing plant. Pan charge, 215 lbs.; 1 lb. KCN per ton of ore; six hours' treatment; 200-mesh pulp. Results: Precipitated as amalgam, gold 96.76 per cent; silver 87.7 per cent; monetary values 95.6 per cent. Shortly after the mill was turned over to the Ruth company, three pans being used, each with 7½-ton charges, the mill foreman's samples and his assayer's results showed as follows: Precipitated as amalgam, gold 96.66 per cent; silver 87.77 per cent; monetary values 95.09 per cent; 1 lb. KCN per ton of ore, six hours' treatment; value of ore \$18 per ton.

Maginnis mill, Maiden, Montana.—One pan; 7½-ton charge; 30-mesh pulp. Oxidized ores containing 0.33 to 0.50 oz. gold and from 1.5 to 4 oz. of silver per ton, contaminated with carbonates of lead, zinc and copper. One pound KCN per ton; 2½ hours' treatment. Precipitated as amalgam, 86 to 92 per cent gold, 62 to 72 per cent silver. The low silver contents of this ore prohibited the economic use of cyanide salt in stronger solutions, in order to secure higher extraction from its silver minerals.

Gold ores from Kendal, Fergus County, Montana.—Decomposed, porous limestone, impregnated with gold; an ideal cyanide ore. Test of 225 lbs. in testing pan; 12-mesh; 1 lb. KCN per ton; after one hour, 90.5 per cent of gold as amalgam; after 2½ hours, 97 per cent of gold contents of the ore reduced to amalgam. Ore valued at \$8 per ton in gold.

Orient, Washington.—Auriferous, fine crystals of pyrite in andesite; no free gold. Average value, 1.03 oz., \$21.29 per ton. Four hours' treatment on 230-lb. lots; 4½ lbs. NaCN; pulp 120-mesh, 95.35 per cent of gold contents saved as amalgam.

Whitman mine, Pearl, Idaho.—Ore contained arsenical pyrites, 25 to 27 per cent; pyrite 40 per cent; gangue 35 to 37 per cent. Six hours' treatment with 4 lbs. KCN; 120-mesh. Gold, 1.3385 oz. per ton, worth \$27.67; saved in form of amalgam, 88.8 per cent.

Metates mine, Sinaloa, Mexico.—Ore contained 5 per cent pyrrhotite, with galena and antimonial sulphide minerals, in quartz gangue. Twelve hours' treatment; 230 lbs., 120-mesh; 12 lbs. KCN used; 7.7 lbs. consumed. Gold, 0.625 oz.; silver, 63.015 oz.; value, \$44.43 per ton. Extracted in form of amalgam, 99 per cent gold, 91.1 per cent silver.

All of the results cited above were obtained by direct pan treatment, without returning any solution once passed through the pan.

MONEL METAL.*

By RICHARD H. GAINES.

HISTORY.

About seven years ago, one of the large smelting companies began investigating the chemical and physical properties of an alloy that had been reduced directly from a nickel-copper matte, without the previous separation of the two metals. This alloy was found to possess not only the more valuable properties of nickel, but other desirable properties in addition, that would ensure a wide usefulness, and owing to the simple method of production, was obtainable at about one-third the cost of nickel. The alloy consists primarily of nickel and copper in the proportion of three parts of nickel to one part of copper, this being the proportion in which the two metals are found together in nature in the great deposits of nickel ore at Copper Cliff in Canada.

The old Swedish and German miners supposed the mineral k  pferrnickel to be a counterfeit or base ore of copper. A fuller knowledge of nickel led to its being better appreciated, and it is now worth nearly three times as much as copper.

Nickel and copper are associated in enormous pyrrhotite deposits in the Sudbury district of Ontario, Canada, and one of the most difficult problems in the treatment of these ores has been that of separating the two metals. In 1905-6, the International Nickel Co., considering, no doubt, that for many purposes there was no need to separate the amicable metals nickel and copper, took up the problem of reducing them together and obtaining an alloy of the two metals in the proportions in which they occur in the ore. The method adopted consists merely in eliminating the impurities, except a small percentage of reduced iron and a minor quantity of other substances which remain with the alloy.

PROCESS OF MANUFACTURE.

Synopsis.—The ore from the mines is first reduced to a matter, which is blown until the iron is nearly eliminated, the sulphur is removed by roasting, and the combined oxides remaining are reduced to metal. The general method of production includes roasting the ore in heaps, followed by smelting in a blast furnace, and further enriching in a converter, which yields a high-grade matte containing about 80 per cent nickel and copper, from 1-2 per cent iron, and the rest sulphur. By careful attention to the furnace charge, it now is claimed that a Bessemer matte can be produced within 1 per cent of the required proportion. The rich matte is shipped to the Orford refinery, where it is ground and roasted in hand rabbled reverberatory furnaces to remove the sulphur, carbonate of soda being used to finish the elimination of the sulphur. The product should be oxides of nickel and copper, with a small proportion of iron, and only a trace of sulphur. This is charged with charcoal into

a reverberatory melting furnace fired with oil. The nickel and copper oxides are thus reduced to metal, and melted.

The alloy thus obtained was found to possess such valuable properties as would ensure it a very wide use on its own account. It was named Monel metal after Mr. Ambrose Monel, the president of the International Nickel Co.

COMPOSITION.

The ores of the Sudbury district vary both in the amount and proportion of nickel and copper, and, therefore, the proportions of these two metals in the alloy will vary within certain limits with the composition of the ore treated. The ore from which the Monel metal is derived contains generally about 4.85 per cent of nickel to about 1.75 per cent copper. When this ore, as it occurs in nature, is reduced to metal, the resulting alloy contains from 66-70 per cent nickel, from 23-28 per cent copper and from 3-5 per cent of other metals, including iron, and a small proportion of manganese.

C. F. Burgess and James Aston¹ give the following analysis of a sample of Monel metal examined in 1909:

	Per cent.
Nickel	67.96
Copper	26.00
Iron	2.80
Manganese	1.62

Analyses of Monel metal quoted by A. Stansfield,² C. E., in *Transactions of the Canadian Society of Civil Engineers* are as follows:

	Cast bar.	Rolled bar.
Nickel	68.90	57.55
Copper	26.55	26.25
Iron	3.30	3.25

On looking through the literature of the subject, no very recent analyses were found. The analyses of cast, rolled, and forged metal (given on page 33) were made at the laboratory of the Board of Water Supply, New York City, during the latter half of 1911.

For such a material as Monel metal, which is not a pure alloy, the feature of these analyses is the remarkable approach to uniformity in composition. If compared with the earlier published analyses, it would appear that the manufacturers have perfected the methods of reduction from ore and matte to such a degree as nearly to control the composition. In the present process of manufacture, the claim is made that the physical properties of Monel metal are not materially affected within the limits of variation in which the constituents occur. If this is true, a closer uniformity in the results of physical tests must be looked for from improvements in the heat treatment. As a matter of fact, the effect of variation in the copper-nickel ratio, as well as the influences of the presence of varying amounts of carbon, iron, silicon and manganese have not hitherto been studied, and are, therefore, not yet understood. A comparison of the

¹Metallurgical and Chem. Eng., 8, 452.

²Canadian Society of Civil Engineers, Transactions, 23, 302-309 (1909).

³A. H. Hiorns, on "Copper-Nickel Alloys," in Metal Industry, August and September, 1911.

*From the Journal of Industrial and Engineering Chemistry.

chemical analyses with the physical tests made at the laboratory affords some deductions.

NICKEL-COPPER RATIO.

On looking over the results of the physical tests, it would seem that the variations found bear little relation to the chemical composition. Specimens of the cast metal in which the nickel-copper ratio was about the same, and other constituents in close agreement, gave a considerable difference in strength and yield point. For example, the specimen from heat 307 showed an ultimate strength of 69,100, and elastic limit 38,450, with a nickel-copper ratio of 68.49-27.02, while the specimen from heat 312 with a nickel-copper ratio of 68.10-27.04 and other constituents nearly identical, gave an ultimate strength of 73,750, and elastic limit 44,550. The difference of 10 per cent in ultimate strength and 15 per cent in elastic limit here is plainly due to some other causes than composition.

CARBON.

In accordance with previous examinations of this material, only the total carbon was determined in the samples submitted. With respect to the influence of this element, tests 275, No. 1, gave ultimate strength 85,250, yield 51,250, and carbon 0.28. Same test, No. 2, showed ultimate strength 86,200, yield 58,250 and carbon 0.44, with other chemical constituents agreeing closely. Same test, No. 4, representing only a different section from the same rod, gave ultimate strength 85,500, yield 51,300, with carbon 0.37. The ultimate strength and yield in these three cases appear to follow in some measure the carbon content. In future study of Monel metal, it would be well to ascertain the carbon relations, for unless it is known in what form the carbon exists in the metal (whether free or combined, and in what ratio) it is fruitless to attempt deductions.

SILICON AND MANGANESE.

In the narrow limits of variation in which these metals were found, no indication was observed of any material effect on physical properties. Manganese is an advantage as a dioxidizer, and it serves a useful purpose in rendering harmless any sulphur that might be present, forming as it would manganese sulphide.

The results of the analyses in general show that the chemical composition alone is an insufficient guide to the strength or other physical properties of Monel metal, which depend, as in steel, so largely upon other influences, and especially heat treatment. Much light on these could be obtained from investigation with the microscope. A metallographic examination of the structure of the various specimens under test would be of great assistance in revealing segregation, the form in which the carbon is present, and other facts having an important bearing on the physical and chemical constitution of the metal.

While the laws governing the nickel-copper alloys are not thoroughly understood, some progress has been made in this study. There are no chemical compounds of copper and nickel, neither is there any eutectic mixture. The metals unite in all proportions without any separation on cooling. Hence, it is inferred that the two metals form solid solutions or mixed crystals in all proportions.

Working with pure metals, Hiorns³ found that nickel dissolves in copper up to a certain percentage forming homogeneous solid solutions, and, on the other hand, taking nickel as the solvent, copper dissolves in nickel, forming homogeneous solid solutions up to a certain limit. These two solutions are miscible in all proportions. These facts have a direct bearing on observations made by David H. Brown,⁴ metallurgist of the Canadian Copper Co., after five years'

ANALYSES OF CAST MONEL METAL.*

Samples taken at the foundry of the Bayonne Casting Co., Bayonne, N. J.
Per cent.

Lab. No.	Description.	Copper.	Carbon.	Iron.	Nickel.	Silicon.	Manganese.	Cobalt.	Total.
1146	Heat 301.....	26.59	0.27	3.19	68.22	1.10	0.26	Trace	99.63
1147	Heat 307.....	27.02	0.31	2.40	68.49	1.08	0.49	Trace	99.79
1148	Heat 308.....	26.59	0.43	2.87	68.23	1.24	0.44	Trace	99.80
1149	Heat 312.....	27.04	0.39	2.68	68.10	1.17	0.37	Trace	99.75
1150	Heat 315.....	27.27	0.39	2.40	68.50	1.23	0.09		99.88
1151	Heat 318.....	26.81	0.38	2.54	68.30	1.36	0.23		99.62
1152	Heat 329.....	27.53	0.31	2.16	68.28	1.41	0.14		99.83
1153	Heat 335.....	27.38	0.25	3.33	68.46	1.24	0.11		99.77

ANALYSES OF ROLLED MONEL METAL.

Samples taken at the foundry of the Bayonne Casting Co., Bayonne, N. J.
Per cent.

Lab. No.	Description.	Copper.	Carbon.	Iron.	Nickel.	Silicon.	Manganese.	Cobalt.	Total.
1154, No. 1	Test 275.....	26.57	0.28	2.09	69.04	0.16	1.32	Trace	99.46
1155, No. 2	Test 275.....	26.71	0.44	2.11	68.81	0.17	1.35	Trace	99.59
1156, No. 4	Test 275.....	26.99	0.37	2.07	68.89	0.18	1.26	Trace	99.76
1157, No. 6	Test 275.....	24.76	0.33	2.44	69.83	0.37	1.82	Trace	99.55
1158, No. 7	Test 275.....	26.94	0.39	2.16	68.48	0.12	1.54	Trace	99.63
1159, No. 8	Test 275.....	26.21	0.43	2.41	68.63	0.20	1.73	Trace	99.61

ANALYSES OF FORGED MONEL METAL.

Sample submitted by the Bayonne Casting Co., Apr. 6, 1911.

Per cent.

Lab. No.	Description.	Copper.	Nickel.	Manganese.	Iron.	Carbon.	Total.
1021	Specimen taken midway between center and outside of billet	26.69	69.45	1.38	2.13	0.19	99.84
1022	Specimen from center of billet.....	26.78	69.52	1.50	2.14	0.17	100.11
1023	Specimen from outside of billet.....	26.83	69.54	1.48	2.19	0.18	100.23

*From the Journal of the Industrial and Engineering Chemistry.

study of copper matte and copper-nickel matte in the Bessemer converter, and in the manufacture of Monel metal. He submits the following conclusions:

1. Nickel-copper alloys act in the matte-blow like one metal.

2. Nickel-copper alloys follow during the matte-blow exactly the same laws that govern the behavior of copper alone.

Browne presents much data to prove that copper-nickel alloys form, as far as conversion is concerned, one homogeneous metal. In conversion, copper and nickel act together, presenting the same curious resistance to oxidation, and their relations toward iron are exactly similar to the relations of copper alone. The resistance to oxidation in the converter may be in some way connected with the resistance of the finished Monel metal to oxidation and corrosion. These facts seem to suggest the idea that the metal is an entity by itself.

As the component metals have never been separated from each other, the particles of each seem to be in more intimate contact than can be attained by any synthetic method of manufacture. It is claimed that melting the constituent metals together has produced no alloy having the same physical properties as the Monel metal obtained direct from the matte. The metal must therefore owe some of its remarkable properties to the grouping of its constituents. Small quantities of foreign substances which ordinarily affect the structure of alloys in general may be of negligible effects in an alloy of this type.

In certain of its chemical as well as physical properties, Monel metal closely resembles nickel. It is slowly dissolved by hydrochloric acid and by sulphuric acid, but dissolves rapidly in nitric acid with the evolution of nitric oxide. It is apparently unaffected by alkalies and shows the same stability as nickel in the presence of other corrosive chemicals. Like both nickel and iron, Monel metal is magnetic, a property which it loses above a certain temperature. Like nickel and iron, it absorbs carbon, and like steel, its physical properties are profoundly influenced, not only by the percentage of carbon, but the form in which it exists in the metal.

In the examination of Monel metal at the laboratory, the carbon present was observed in some samples in the free form as graphite, and in a smaller degree as combined carbon, the differential relations apparently depending as in iron on the rate of cooling.

PROPERTIES.

In appearance, Monel metal resembles nickel in color. It takes a brilliant polish, nearly equal to that of silver, which it retains indefinitely. On long exposure, the surface assumes a grayish cast, which may be removed with a polishing cloth. It is somewhat

tougher than mild steel, but, nevertheless, it machines very easily. A lathe can be run at about the same speed on Monel metal as on mild steel, and the metal can be soldered, brazed, electrically welded, and successfully drawn.

SOME OF THE PHYSICAL CONSTANTS OF MONEL METAL ⁶	
Melting point.....	1360° C. or 2480° F.
Specific gravity (cast).....	8.87
Weight per cu. in. (cast).....	0.319 lb.
Weight per cu. in. (rolled).....	0.323 lb.
Coefficient of expansion, 20° to 100° C.	0.00001375 per 1° C.
Electrical resistivity temperature coefficient 0.0011 per 1° F.=256 ohms per mil-foot.	
Electrical conductivity (copper 100 per cent)	4 per cent.
Heat conductivity.....	1/2 of that of copper.
Shrinkage	1/4 inch per foot.
Hardness, cast material (Shore scleroscope)	20 to 23
Hardness, hot rolled rods (average Shore scleroscope).....	27

A comparison of some of the properties of copper, nickel and Monel metal, as reported by a recent authority,⁸ is given below:

	Monel metal.			
	Copper rolled.	Nickel rolled.	Cast.	Ann'l'd.
Tensile strength, lbs. per square inch.....	34,000	75,500	85,000	100,000 110,000
Elastic limit, lbs. per square inch.....	18,000	21,000	40,000	50,000 80,000
Elongation in 2 inches per cent.....	52	43.9	25	30 25
Contraction, per cent.	57	57	25	50 50
Melting point.....	1084°C.	1500°C.	1360°C.	

Recent tests⁷ of Monel metal at laboratory of William Sellers, Philadelphia, Pa., are:

	Hot rolled rods.	Sand castings.
Elastic limit, lbs. per sq. in.....	58,873	37,427
Breaking strength, lbs. per sq. in.....	86,899	78,236
Elongation in 2 inches, per cent.....	40.0	38.5
Reduction of area, per cent.....	60.5	34.0
Modulus of elasticity.....	22,000,000 to 23,000,000	

In all the technical reports relating to Monel metal, it is referred to as a non-corrosive alloy. Redfield⁸ and other writers claim that the castings have the strength and many other properties of cast steel, while they have greater resistance to corrosion from sea water, superheated steam and corrosive chemical solutions than the bronzes. Owing to its remarkable stability in sea water, the government is now equipping its battleships with propellers of this material, these being cast in single pieces. Propellers have already been made for the North Dakota and for battleships of other countries, some of the latter being 15 ft. 6 in. in diameter in a single piece, weighing 16,000 lbs. After 18 months' service, it is said that the wear and corrosion of these propellers was found to be practically negligible. It was further found that they resist bending to such an extent that they are not so subject to loss of efficiency as propellers which yield under heavy backward pressure against the water.

Experiments made at the laboratory indicate that Monel metal possesses about the same resistance to corrosive action as the better known bronzes. Specimens of several bronzes, Monel metal, and steel were weighed and embedded in rich earth, which was kept wet for six months by periodical additions of very dilute solutions of corrosive salts. At the end of the

⁶Mining World, 30, 470.

⁷Physical data in part from John F. Thompson, in Eng. and Mining Journal, 91, 1911.

⁸Transactions of the American Institute of Mining Engineers, 41, 310 (1910).

⁹Ibid., 1911.

⁸S. B. Redfield, American Machinist, 34, I, 513-514.

test period all the specimens were taken out, scrubbed, dried and weighed to ascertain the comparative loss from corrosion. The results were as follows:

	Per cent loss.
Phosphor bronze.....	0.09
Tobin bronze.....	0.11
Monel metal.....	0.12
Parsons manganese bronze.....	0.12
Muntz metal.....	0.33
Steel	1.04

Another test of the same kind, under somewhat different conditions, but the same period, gave about the same relative results.

One advantage in favor of Monel metal in these tests was that it presented the least change in appearance as a result of the corrosive action.

CASTING.

While no trouble has been experienced in rolling Monel metal, considerable difficulty has been met with in some foundries in getting sound castings. Incidentally, it may be remarked that nickel-copper alloys have a great tendency to develop blow-holes on casting, due to occluded gases. This is another indication of the absence of a chemical compound, since the presence of a compound in an alloy seems to have the influence of preventing blow-holes, and closing the grain. Monel metal requires special precautions in casting on account of dissolved oxides and gases, which, if not removed, would render the ingots unsound. Successful castings have been made in small foundries by adding 2 ounces of magnesium per 100 lbs. of the alloy, before pouring.

Unsound castings may also arise from gases that are liberated in the cores of the patterns, and from the fact that the freezing point of the metal is so many hundred degrees above that of brass or bronze that these gases cannot escape before they are trapped by the freezing metal. This necessitates the use of the same methods as for fine steel castings. It must be remembered that the actual temperature of Monel metal cannot be much lower than 1550° C. The art of casting Monel metal is closely related to the art of casting steel, as distinct from the art of casting brass, bronze or cast iron. It really involves the art of handling the finest steel castings. The practice of casting Monel metal is, therefore, very similar to that followed in steel foundries. The melting equipment of the plant consists of standard reverberatory furnaces which are fired with oil, the fuel being fed by gravity. The metal is charged into the furnace in the form of pigs or slabs which are about 15 × 8 × 3 inches in dimensions, and weigh about 85 lbs. The melting point is about 2500° F. and eight hours are required to the heat. No fluxes nor alloys are necessary. Because of the relatively scant knowledge of nickel and its peculiarities, the handling of Monel metal requires expert attention in the melting.

The industry of making Monel metal castings is now past the experimental stage, and is being successfully accomplished in at least three foundries in New

York and New Jersey. Mr. Leonard Waldo, consulting engineer, is authority for the statement that notable success has been achieved at the Johnson Foundry of Spuyten Duyvil in the casting of this metal. The Bayonne Casting Co., of Bayonne, N. J., and the Riverside Steel Co., of Newark, N. J., are other foundries that are making good castings.

USES.

Although a comparatively new alloy, because of its resistance to corrosion, its strength and the readiness with which it may be machined, Monel metal has already found many important uses. These include pump cylinders for handling salt water, propeller wheels, rudders, centre boards, deck fittings, mining screens, water ends of pumps, linings, valves, shafts, piston rods and plumbing fixtures subject to corrosive influences.

In the rolled metal, there is a wide range of usage. Striking instances in the past include the roofs of the new terminals of the Pennsylvania Railroad in New York, and the Chicago & Northwestern Railroad in Chicago, which were covered with Monel metal. The sheets have also been used on several large office buildings in New York, and on industrial plants subject to severe corrosive conditions where copper had proved unsatisfactory.

Rigid physical specifications should be the rule wherever Monel metal is considered for use in any form of engineering construction. With reference to chemical specifications, it would be impracticable to set any narrow limits as to chemical constituents, owing to the somewhat variable character of the ore and the method of manufacture. It is not believed, moreover, that such limits are necessary in order to insure the desired physical properties of strength and durability. If too close limits are set on chemical constituents, the metal so specified might be obtained, but at a cost that would render its use prohibitory.

The problem of making Sweden independent of foreign coal has lately been receiving much attention, according to U. S. Consular Report, and experiments have been made with peat from bogs in northern Sweden. The peat was permitted to dry one summer and then crushed to a fine powder. This is further dried in ovens containing several sections, the hottest section being on top. Heating requires 20 minutes, which makes the pulverized peat black and reduces the water content to 15 per cent. The ovens have a capacity of 25 tons daily, and are fired with the powder, which sells at the factory for \$2.27 per ton. It may also be used for boilers, and the state railway authorities are experimenting with it. The report states that generally the tests have not proved satisfactory from an economic and business point.

Among the industrial scholarships recently announced by the University of Pittsburgh is one in the chemistry of baking.



METHODS OF ANALYSIS FROM THE LABORATORIES OF ARMOUR INSTITUTE OF TECHNOLOGY.

IV.

THE DETERMINATION OF LEAD IN ORES.

The analytical determination of lead in natural bodies would be a very simple matter were it not for the fact that most lead ores contain calcium compounds, and that many calcium compounds resemble the corresponding lead compounds in solubility and in general chemical behavior.

The separation of lead from the other heavy metals, and in fact from all the metals which accompany it in nature except the metals of the alkaline earths, is readily effected through the insolubility in dilute sulphuric acid and its sulphate, and its determination either gravimetrically or volumetrically is correspondingly simple.

The methods to be described are applicable to ores carrying calcium and iron. The steps in the processes which may be omitted if alkaline earths are known to be absent will be indicated later.

THE GRAVAMETRIC DETERMINATION OF LEAD IN ORES.

The 0.5 gm. samples are digested on the hot plate in 250 cc. Erlenmeyer flasks with concentrated HCl until the residue is white. If complete decomposition does not take place in reasonable time, a few cc. of $KMnO_4$ are added to the HCl. When decomposition is complete, flask and contents are cooled, 8 cc. of concentrated H_2SO_4 added, and the whole evaporated to copious fumes of sulphur trioxide, HNO_3 and HCl being eliminated and silicic acid dehydrated. After cooling, about 100 cc. of water are added, the flask rotated and allowed to stand a few moments, when the insoluble residue containing $PbSO_4$, $CaSO_4$ and the gangue of the ore is filtered off and washed with cold 5% H_2SO_4 . If the residue is large, it need not all be transferred to the paper. It is, indeed, more convenient to retain the bulk of it in the flask, washing it several times by decantation. When the washing is complete, the filtrate is discarded, the flask containing the bulk of the precipitate placed under the filter, and the paper washed with a hot concentrated solution of ammonium acetate acid with acetic acid. The contents of the flask are heated, and then poured over the same filter, where the residue is washed with ammonium acetate until a few drops of washings give no dark precipitate with $(NH_4)_2S$. This treatment separates the gangue as a white residue and leaves lead and calcium in acetate solution, from which the lead is precipitated completely after dilution, by hydro-

gen sulphide. The PbS is filtered off and washed until the washings contain no calcium (as shown by test with ammonia and ammonium oxalate). It is then dissolved into a 250 cc. beaker by a stream of hot 1:1 HCl containing NH_4Cl from a wash bottle, 8 cc. of concentrated H_2SO_4 added, and the whole run down to dense fumes of SO_3 on the hot plate. After cooling, 100 cc. of water are added and a little alcohol and the whole allowed to stand until cold. The $PbSO_4$ is thrown on a tared Gooch crucible washed with dilute H_2SO_4 (5%) and finally with alcohol, dried, ignited at a dull red by heating the Gooch inside of a larger iron or porcelain crucible or directly in a muffle, and weighed as $PbSO_4$.

$$\text{gms. } PbSO_4 \times 0.6831 = \text{gram. Pb.}$$

$$\text{gm. Pb.}$$

$$\frac{\text{gm. Pb.}}{\text{weight of sample}} \times 100 = \% \text{ Pb.}$$

weight of sample

If it is inconvenient to use a Gooch crucible, the precipitate of $PbSO_4$ may be filtered upon a special paper, dried, removed as cleanly as possible from the paper, the paper burned, the main precipitate added, and the whole ignited at a dull red heat after the addition of a drop of nitric acid and one of sulphuric. A porcelain crucible should be used. For small quantities of $PbSO_4$ precipitate, the burning of filter and precipitate together may be successfully accomplished in a muffle, the $PbSO_4$ coming out white and pure. The writer has frequently done this in platinum without harm to the crucible, but does not recommend the use of platinum.

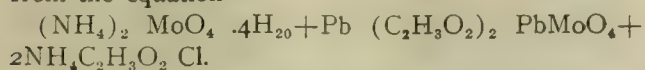
THE VOLUMETRIC DETERMINATION OF LEAD.

This method depends upon the fact that ammonium molybdate throws down from acetic acid solution, a white precipitate, very insoluble, of $PbMoO_4$, the end point of the titration being the brown color produced when the first excess of ammonium molybdate is brought in contact with a fresh solution of tannic acid. The indicator must be used externally. Interfering elements are notably calcium and iron. The calcium stays with the lead when the latter is precipitated as sulphate, and if present in the solution titrated would give a precipitate of calcium molybdate just as the lead salt is formed, yielding, of course, high results. Iron must be absent, for where even a small quantity is present the dark tannate of iron (ink) would obscure the end reaction.

PREPARATION AND STANDARDIZATION OF SOLUTION.

The molybdate solution is ordinarily made of such strength that 1 cc. = about 0.005 gms., so that, when a 0.5 gm. sample of ore is used, the burette reads the

approximate per centage of lead direct. Calculating from the equation



the weight of molybdate corresponding to 0.005 gm. Pb is found to be 0.00425 gm., so a litre of solution of this strength would contain about 4.25 gm. of the crystallized salt.*

Samples of 0.2 gm. weight of clean, pure lead foil are weighed out and dissolved in a few cc. of nitric acid (1:1) the solution being evaporated to dryness. The lead nitrate is taken up in water (50 cc.) and 5 cc. H_2SO_4 added, the solution shaken, cooled, allowed to settle and the $PbSO_4$ filtered off and washed with cold dilute 5% H_2SO_4 . The paper carrying the precipitate is returned to the original flask where it is boiled with 10 cc. concentrated HCl until completely disintegrated. To this 15 cc. more of strong acid are added, the whole made alkaline with strong NH_4OH , and finally acid with acetic acid. After dilution to about 250 cc., the solution is boiled and titrated immediately.

In titrating, it is well to pour the greater part of the solution into a beaker, retaining a portion in the original flask. Molybdate solution is run into the solution in the beaker until the end point is past, more lead solution added, and the end point again passed. This is continued until the final rinsing out of the flask leaves the solution very near its end point, when the titration is finished two drops at the time. If, after the end reaction appears in the final test, it appears, after standing, in some of the previous tests, 0.1 cc. is deducted from the last reading for each test that shows the brown color.

Weight of lead

————— = lead value of solution
Corrected volume of solution
per cc.

The indicator is 1% tannic acid solution, and should be fresh. It is used, of course, outside of the main reaction, on a "spot plate."

The Determination—Half gram samples in 250 cc. Erlenmeyer flasks are treated with 10 cc. concentrated HCl and boiled until H_2S is completely expelled. If the residue is dark, a few cc. of nitric acid are added and the boiling continued until the gangue is white, when 7 cc. concentrated H_2SO_4 are added and the solution evaporated to dense fumes of sulphur trioxide. After cooling, the whole is diluted to 60-70 cc., boiled, allowed to cool and the precipitate to settle, filtered and washed with cold 5% H_2SO_4 . The precipitate is $PbSO_4$ contaminated with $CaSO_4$ the gangue, and traces of ferric sulphate which are almost impossible of removal by washing. The precipitate is rinsed back into the flask by a stream of water from the wash bottle, and about 30 cc. of 20% SH_4Cl solution acidified with HCl poured through

the paper into the flask. The contents of the flask are boiled until the lead and calcium sulphates are dissolved leaving only the gangue as a residue, which may be readily recognized as such, and the lead precipitated as PbS by the addition of an excess of ammonium sulphide solution. After boiling, the PbS is filtered off and washed. This treatment effects a clean separation of the lead from calcium, but traces of iron as FeS are likely still to be present. To remove these traces of iron, which if present would give a dark color with the tannic acid indicator, and so obscure the end point of the titration, the PbS is rinsed from the filter paper into the original flask, where it is thoroughly agitated with 10 cc. of 5% solution of H_2SO_4 , after which H_2S water is added to reprecipitate any traces of lead which might have gone into solution, the precipitate allowed to settle, filtered off and washed with cold water.

Filter paper and PbS are now placed in the flask and boiled with 5 to 10 cc. of strong HCl until the paper is disintegrated and the PbS completely converted to chloride, a few drops of HNO_3 being added to oxidize any dissolved H_2S . The solution is diluted with 25 cc. of water, a piece of libnus paper added, and then ammonia water to alkaline reaction is added and finally, acetic acid until distinctly acid. After dilution to 200-250 cc., the solution is titrated hot with molybdate solution just as in standardizing.

$$\frac{\text{cc. of solution used} \times \text{lead standard}}{\text{weight of sample}} \times 100 = \% Pb$$

In lead products which are known to contain no calcium, both gravametric and volumetric methods may be much simplified.

In the gravametric process, the ore is treated exactly as previously described through the first filtration and washing of the residue containing $PbSO_4$ and gangue. The residue is treated with ammonium acetate acid with acetic acid, as before, but in this case, the $CoSO_4$ being absent, only $PbSO_4$ is dissolved. The filtrate containing the lead is boiled, and after dilution to 75-100 cc., 10 cc. of concentrated sulphuric acid are added, followed by some alcohol. After cooling and settling the $PbSO_4$ is filtered off on a weighed Groch crucible, washed, ignited and weighed as described.

In the absence of calcium, and especially if lead is low, the sample of ore may be prepared for the titration of its lead by molybdate solution in a much simpler way. The decomposition of the ore is exactly as described, and the treatment the same through the solution of the first precipitate of $PbSO_4$ in MH_4Cl and HCl. Instead of the precipitation of PbS at this point, the procedure is as follows: 15 cc. more of HCl are added, 25 cc. of water and thus 25 cc. of strong ammonia solution. A bit of litmus paper is dropped in the flask, the solution made alkaline with ammonia and then acid with acetic acid, diluted to 200 to 250 cc. boiled and titrated as before.

*Common ammonium molybdate is not $(NH_4)_2 MoO_4$, but $(NH_4)_6 Mo_7 O_{24}$. The simplest formula, approximately correct, is generally used.

In the absence of calcium, and when lead is low and iron low, this method is pretty satisfactory. If lead is very high, however, the large bulk of PbSO_4 precipitate clings so tightly to small quantities of ferric sulphate as to carry enough ferric salt with the final titration to interfere with the end reaction by forming a dark color with tannic acid.

For unknown ores or, indeed, for any ores, when the best results are desired the full purification of the lead should be carried out.

THE CALCIUM CARBID METHOD FOR DETERMINING MOISTURE

Calcium carbid was used as a dehydrating agent in obtaining absolute alcohol as early as 1897, by P. Yvon.¹ H. A. Danne in 1900 described before the Society of Chemical Industry of Victoria a method for determining moisture, by heating the substance under examination, passing the water vapor through calcium carbid, and measuring the gas obtained. P. V. Dupré used a similar method in the study of ammonium oxalate,² and cordite,³ and Cripps and Brown⁴ applied it to spices. Roberts and Fraser⁵ used calcium carbid to determine water in an emulsion of crude petroleum by adding the carbid directly to the emulsion and measuring the gas given off. Irvine Masson⁶ heated calcium carbid in direct contact with a number of substances in a study of the effect on water of crystallization.⁷ Recently Rivett⁸ has used the same method for moisture in butter, allowing the acetylene to escape and estimating its amount by loss in weight of the apparatus.

APPARATUS AND METHOD.

The hope that calcium carbid heated with the material to be analyzed might in some instances afford a more satisfactory means of determining the water present than those now available, led to an investigation by the Bureau of Chemistry of the U. S. Department of Agriculture. The results of this investigation are set forth as follows by Mr. H. C. McNeil, of the Contrasts Laboratory, in a circular issued recently by the Bureau: After a number of pieces of apparatus had been set up and tested, the arrangement shown in Fig. 1 was adopted and is now in use. As there shown A is the generating flask of about 25 cc. capacity into which the material to be analyzed is weighed; B is the carbid tube with a projection on one side for holding 5 cc. or more of the carbid; C is a 100 cc burette drawn out at the ends to facilitate connections, and is jacketed and the jacket connected with the tap at D for the purpose of rapid cooling and accurate control of temperature; E is the leveling vessel. The liquid used in C and E is mercury or a

concentrated solution of sodium chlorid in water, which has stood in contact with acetylene until saturated, and is tinted by means of phenolphthalein and a little sodium hydroxid to facilitate reading.

To operate, introduce a weighed amount of the sample into A. If this is not in powder form it is advisable to add barium sulphate, silica, or similar substance and fine sand and mix until the whole is a dry powder, so that the carbid can be brought easily into contact with all parts of the original material, or, the sample may be dissolved or suspended in a suitable liquid and treated with the carbid in this form. Charge tube B by filling the side projection with the

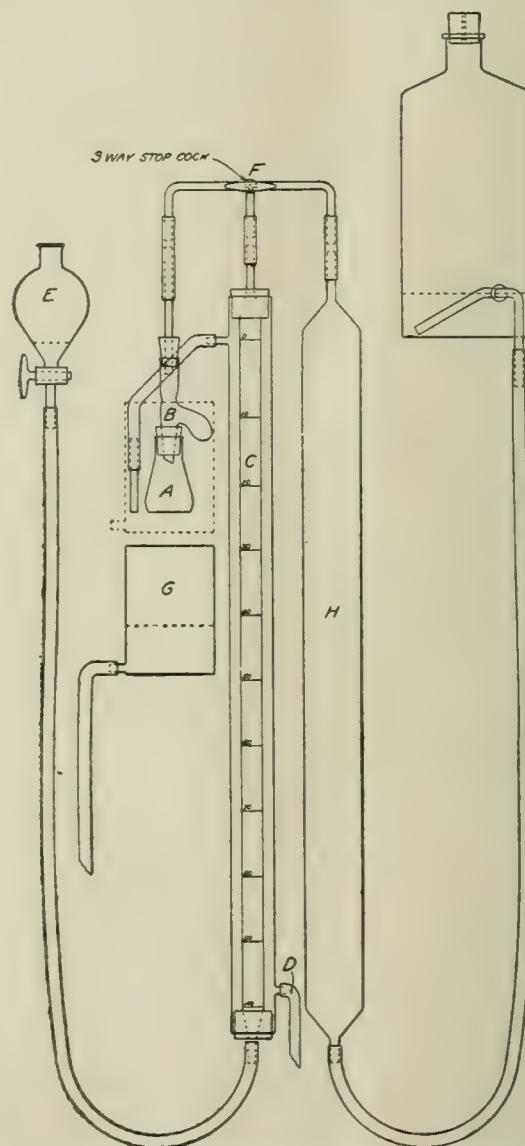


Fig. 1—Apparatus for Determination of Moisture by Calcium Carbide Method.

carbide which has been ground in a ball mill to a fine powder. Push a plug of cotton down the vertical part of the tube to the constriction above the projection and place a little carbide above the cotton, holding it in place by another small plug of cotton, and alternate until the tube is loosely filled with carbide and cotton, thus preventing the escape of any moisture volatilized by the heat of reaction, which is

¹Compt. rend., 1897, 125; 1181.

²Analyst, 1905; 30:266.

³Analyst, 1906, 31:213.

⁴Analyst, 1909, 34:519.

⁵J. Soc. Chem. Ind., 1910, 29:197.

⁶J. Chem. Soc., 1910, 97:851.

⁷See also Chem. News, 1911, 103:37.

⁸Chem. News, 1911, 104:261.

great. Then connect *B* with *C* and *A* with *B* by means of snugly-fitting rubber stoppers and rubber tubing as shown in the cut, no other support being necessary. Open the three-way stopcock *F* to the air by pulling it partly out, and bring the vessel *G* up around *A* so that *A* can be entirely surrounded by water. Allow tap water to run through the jacket about *C* and into *G*, where its height may be maintained as desired by drawing off at the outflow near the bottom of *G*. When the apparatus has cooled to the temperature of the tap water bring the liquid in tube *C* to the zero mark by raising or lowering *E*, turn *F* so as to allow *A* and *B* to communicate with *C*. Lower *G* and introduce a small amount of carbid into *A* by tipping *B* to one side. The rate of reaction is controlled by the rate of admission of the carbid. Keep the level of the water in tube *C* and bulb *E* as nearly the same as possible, by lowering *E* as necessary. When all of the carbid has been added and thoroughly mixed by shaking and rotating the bulb *A*, an easy operation because of the flexible nature of the connection, place a vessel of water in the position formerly occupied by *G*, bring this water to a boil and maintain as long as gas continues to be generated, usually not more than 10 or 15 minutes. In some experiments a glycerin bath has been used, and heated in a few cases as high as 130° C.

When the reaction is over remove the water bath, replace the vessel *G*, and when the apparatus is of the same temperature as in the beginning read off the volume and reduce to standard conditions. Read the temperature of the tap water as recorded by a thermometer suspended in vessel *G*. Ice water was used in some experiments, but the condensation of moisture on the outside of the jacket was objectionable and its use was abandoned. The tube *H* in the apparatus here shown is an auxiliary container, holding about 1,000 cc, for use when the material under examination contains a high per cent of moisture or is of such a nature that a fair sample can not be obtained in gram amounts. In such cases turn the stopcock *F* so as to connect both *C* and *H* with *A*, and at the end of the reaction lead the gas from *H* into *C* in suitable portions, cool, measure, and force out of the apparatus. This is easily done by manipulation of *F* and the leveling vessels *E* and *I*, and is greatly facilitated if before beginning the experiment a permanent support for *E* is so placed that the liquid in *C* stands at the 100 cc mark, and a similar support is arranged for *I* so that the liquid in *H* stands at the zero mark. In order to calculate results it is necessary to know how much gas a known amount of water will yield. This should be determined as nearly as possible under the conditions of the moisture determinations.

According to Lunge⁹ 100 grams of calcium carbid yield 40.574 grams (35.019 liters) of acetylene. By this relation, if Moisson's formula ($\text{CaC}_2 + 2\text{H}_2\text{O} =$

$\text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$) holds, 1 gram of water should give 623.17 cc of acetylene at standard conditions. In practice about 580 cc are usually obtained.

One series run in a mercury-filled apparatus yielded 607 cc of acetylene for a set of closely checking results. The first series with the apparatus here described measured over a concentrated sodium chlorid solution that stood in contact with acetylene until saturated with it gave 586 cc, and the latest determinations gave 582 cc. Little difference in results has been noted whether the carbid was added directly to the water in flask *A*, in which case the reaction is too vigorous at first, or whether sand, barium sulphate, or cotton was first mixed with the water. Precipitated silica gave low results, indicating that it held about 0.8 per cent of its own weight of water, but more determinations must be made to confirm this. The reaction was complete at 100° C. in all blanks. Heating to 130° C. has no deleterious effect on the rubber connections, but much above that will injure them and ruin the determination. At these temperatures there was no evidence that the acetylene affected the rubber in any way. A good procedure in many cases is to run a determination and follow with a similar amount of material plus a weighed amount of water. Until the action of calcium carbid on all of the materials present and under different conditions is known, the necessity of running the blanks in exactly the same way as the determination can not be too strongly emphasized. The value for 1 gram of water being found, the percentage of water in the sample is calculated from the result of the determination.

APPLICATION OF THE METHOD TO DETERMINATIONS OF MOISTURE IN PAINTS AND SOAPS.

The determination of moisture in paint and paint material and soaps being constantly before the Contracts Laboratory, the application of the carbid method to these substances was investigated. Dry pigment could be mixed readily with the carbid and presented no difficulty in operation. (1) White lead is not attacked by calcium carbid, and this method gives good results for hygroscopic moisture, the water of composition not being affected. (2) Gypsum did not react until the temperature neared 100° C.; then the reaction ran rapidly, but not quite all of the two molecules of water was removed. Heating to 135° C. gave the same result as at 100° C. (3) Kaolin yielded by the carbid method the same amount of moisture as is indicated by the loss shown on heating to 100-105° C. The water lost at higher temperatures is not affected by calcium carbid. In general, calcium carbid reacts very vigorously with water, but is not reactive in other ways.

Paints or pastes and soaps were mixed with freshly ignited barium sulphate in sufficient quantities to overcome all pastiness; then sand was added to make the mass granular and easily miscible with carbid. After this was accomplished they presented no further operative difficulties. Paints require a large amount

⁹Chemisch-Technische Untersuchungs Methoden, Aufl. 5, 1905, 2:710.

of inert material to bring them into good working condition. Rubbing up firm soaps is a tedious operation, while moist soaps lose perceptible amounts of water in the process; hence suspension in liquid was attempted instead. Several liquids were examined to determine their suitability for this purpose, and the effect, if any, of calcium carbide upon them. Liquids likely to be found in paints or soaps were also subjected to experimental tests.

(1) Gasoline vaporized by the heat of reaction and was not condensed at the temperatures used, usually about 5° C. In other words, gasoline has a large and unknown vapor tension at the temperatures used, and its presence or that of similar volatile oils will prevent the use of this method of determining moisture. A plan for absorbing acetylene and thus separating it from these and similar impurities is being considered.

(2) Kerosene inhibited the reaction and considerable shaking was required to keep it from being unduly prolonged. The vapor pressure was found to be low enough to allow its use as a solvent. Cylinder oil and similar mineral lubricating oils run well and are good liquids to use in determining the moisture in substances dissolved or suspended in them.

(3) Toluene is not acted upon by calcium carbide, and its vapor tension is not sufficient to prevent its use as a solvent of suitable materials. It mixes well with paint vehicles and gives more satisfactory results than any other liquid tried, but the boiling point is rather low, and it vaporizes, condensing, however, on cooling. A rather dry sample of soap was not dissolved readily, and hence the action was too much prolonged.

(4) Oleic acid reacts slowly with calcium carbide at 100° C., yielding acetylene and forming a hard cake removed from the flask only with difficulty. Therefore, it is not suitable as a solvent.

(5) Stearic acid is not attacked by calcium carbide and makes a suitable solvent for some purposes.

(6) Linseed oil is not attacked by calcium carbide. In the presence of water it causes much foaming, and the reaction runs slowly, so that it is not suitable as a solvent, but its presence in paint causes no difficulty.

(7) Turpentine is not attacked by calcium carbide, and its vapor tension is low enough to make it a satisfactory solvent, though the action is somewhat slow in its presence.

(8) Alcohol is not attacked by carbide at its boiling point, but has a considerable vapor tension, for which correction must be made, and it dissolves six times its volume of acetylene at 18° C., which introduces errors not easily overcome. Ordinary alcohol treated with calcium carbide is dehydrated and saturated with acetylene, and this may be used in some cases without introducing errors. Its wide range as a solvent makes it a desirable reagent.

(9) Amyl alcohol is not affected by carbide and has a lower vapor tension and higher boiling point than ethyl alcohol, making it a useful solvent.

(10) Glycerin is attacked by calcium carbide. Gas equivalent to 12 or 14 per cent of water was obtained in excess of hygroscopic moisture known to be present. It can not be used as a solvent, and its presence in any considerable quantity will vitiate the results.

(11) Anilin has no appreciable vapor tension and gives good results on blanks, though the reaction is somewhat prolonged by its presence.

The examination of these liquids shows that with few exceptions their presence will not interfere with a moisture determination by this method, and that some of them are suitable solvents. But experiments with paints and soaps indicate that as a rule more satisfactory results are obtained by mixing the sample with dry, inert material than by solution or suspension in liquids. Soap in fine shavings to which carbide is added yields much of its moisture, but the reaction is completed too slowly even at 130° C. to be of value. Dry, firm samples dissolve incompletely in alcohol and the reaction is slow; moist samples give good solutions and run well. By rubbing up samples with barium sulphate and sand the most concordant results were obtained, but these differed from results given by other methods of moisture determination, carefully carried out by Mr. G. C. Schmidt in this laboratory. For example, in one case this method gave 28.10 per cent, 28.12 per cent, and 28.03 per cent; by evaporating with alcohol (official method), 25.86 per cent and 26.01 per cent; by Fahrion's method (heating in oleic acid), 28.21 per cent; by difference on complete analysis of the soap, 25.77 per cent and 25.88 per cent.

An extensive examination was made of a sample of castile soap to determine the loss in a vacuum desiccator. Three thoroughly-ground samples of about 2 grams each were weighed out and placed in a vacuum desiccator over sulphuric acid and three similar samples were placed in a second desiccator over calcium carbide lumps and evacuated. These were weighed daily for two weeks and weekly for seven weeks longer, fresh acid and carbide being introduced occasionally. The total losses are shown in Table I:

TABLE I.—TOTAL LOSSES OBTAINED BY DRYING CASTILE SOAP IN A VACUUM DESICCATOR FOR VARYING PERIODS.

Agents—	Per cent loss during—					
	1 day.	1 wk.	5 wks.	6 wks.	7 wks.	9 wks.
Sulphuric acid....	6.31	11.12	12.23	12.29	12.29	12.24
Calcium carbide...	6.14	11.15	12.26	12.33	12.36	*12.32

*Two samples.

By proposed carbide method: 11.30 and 11.38 per cent loss was found.

Results obtained by Schmidt with other methods: By evaporating with alcohol, 12.82, 13.48, and 12.95 per cent; by Fahrion's method, 13.95, 13.92, and 13.76 per cent; by heating in dynamo oil, 13.56, 13.55, and 13.14 per cent.

Soap powder and bath powder merely mixed with calcium carbide ran satisfactorily, giving concordant results usually somewhat lower than the loss by drying at 105° C.

A number of infants' foods composed of more or

less lactose were run for moisture. Being dry powders, they were simply mixed with the carbid. Little gas was generated at ordinary temperature, and on boiling the reaction was slow and prolonged, in some cases an hour or more being necessary for its completion. The results by drying in vacuum at 65° C., by drying in vacuum at 100° C., and by the carbid method are given for comparison in Table II:

TABLE II.—COMPARISON OF RESULTS OBTAINED ON DRY POWDERED INFANTS' FOODS BY TWO METHODS.

No.	—Loss in vacuum—		Carbid method.
	At 65° C.	At 100° C.	
994.....	2.5	3.5	2.89 and 2.93
995.....	6.5	7.65	6.52 and 6.55
996.....	1.6	2.4	2.16 and 2.17
997.....	3.2	4.85	4.26 and 4.23

A sample of pure lactose which lost 5.24 per cent on heating three hours at 105° C. gave gas very slowly with carbid. After nearly two hours' boiling an equivalent of only 1.61 per cent of water was obtained.

Determinations upon flour, leather powder, chrome leather powder, vanilla beans, and sawdust have been run satisfactorily and trustworthy results obtained, as shown by comparison with the best methods available. The determination of the water content of fruit juices is at present being investigated. It is believed that calcium carbid has possibilities for the determination of the actual moisture present that warrant a further study of its action under varied conditions.

ITALIAN SHIPMENTS OF CARBON BISULPHIDE.

The United States Consul at Catania, Italy, reports that a shipment of 50 tons of carbon bisulphide has recently been made from Catania to the United States. This shipment, it is learned, is the forerunner of a monthly consignment of like amount. This fact, coupled with several inquiries received from rubber manufacturers, induces the belief that a shortage in the supply of that product exists in the United States. When it is considered that there is a duty of 25 per cent on the product, that owing to its highly inflammable and explosive nature difficulties are encountered in finding vessels which will carry it, that the freight is \$18.25 per ton, that the containers (iron drums) are of two-thirds the value of the product and are subject to a duty of 45 per cent, it must be evident that the seeking of this product in a foreign market is hardly a matter of price, but is the result of inadequate production in the United States. There is one establishment producing bisulphide of carbon at Catania. It began operations some 12 years ago to supply a local and neighborhood demand, where the article is used in extracting the oil remaining in the residue of olive-oil presses. Catania, being a sulphur center, was naturally a desirable location. The local concern quotes prices f. o. b. Catania as follows: \$5.98 per 100 kilos (220.46 pounds) for bisulphide of carbon, and drums (capacity 200 kilos, or 440.92 pounds) at \$7.72.

THE CONSTITUENTS OF CONIFEROUS WOODS.*

By J. F. BRIGGS, A. C. G. I.

The study of the extremely complex question of the nature and constitution of the woody substance of the coniferous woods has been considerably advanced in the last two or three years by the researches of Professor Klason, of Stockholm. In 1911 he published a brochure, setting forth the results obtained from his investigation of the by-products of the manufacture of sulphite wood pulp. According to Klason, dry spruce wood contains about 10 per cent of wood gum, yielding on hydrolysis 25 per cent of pentose, and about 28 per cent of lignin, which, however, is not in chemical combination with the cellulose and other carbohydrates. Lignin is a colloid having apparently a very high molecular weight; it is a mixture of at least two main constituents differing in their proportions of methoxyl groups. These constituents have been formulated by Klason as $C_{40}H_{42}O_{11}$ and $C_{39}H_{40}O_{12}$.

In connection with the sulphite process, Klason has put forward the hypothesis that lignin may be regarded as a condensation product of coniferyl and hydroxyconiferyl alcohols, in which four molecules are condensed together with the elimination of $3H_2O$. This hypothesis certainly gives a simple and apparently a sufficiently complete working picture of the reactions which take place in the sulphite process of digestion of wood, but it has not been sufficiently developed in its general relations to other reactions to be accepted as a final solution of the constitution of the lignin molecule.

Attacking the problem in another direction, likewise in connection with the great Swedish national industry, he has also studied the by-products of the manufacture of wood cellulose by the sulphate process. In this process the wood is digested with a lye containing as active ingredients sodium hydroxide and sodium sulphide, together with sodium sulphate as a restraining agent. The subject was approached by Klason, first from the point of view of the recovery of volatile by-products: oil of turpentine and methyl alcohol. The methyl alcohol is derived from the methoxyl groups of the lignin, and part of it combines by a secondary reaction with the sulphur in the lye, producing methyl mercaptan and methyl disulphide, which are the cause of the abominable odor connected with this branch of the industry.

In a paper recently published by Klason and Segerfelt (German translation in *Der Papierfabrikant*, 1911, 9, 1093), the conditions which favor the production of mercaptan have been studied. It would appear generally that the higher the proportion of total alkali employed for the digestion, the smaller is the proportion of mercaptan produced. This is explained by the fact that the mercaptan is a body with acid function which is partially converted by the excess of

*From The Chemical World.

alkali into dimethyl sulphide, the odor of which is far less powerful. The quantities of methyl mercaptan and dimethyl sulphide therefore tend to vary inversely. Further, it is desirable that the proportion of alkali present in the form of sulphide should not exceed 20-25 per cent of the total alkali.

The authors next turned their attention to the non-volatile by-products derived from the wood. By evaporating the black lyes to a syrup *in vacuo*, saturating them with carbon dioxide and then heating at 110°-120° C., the lignin was separated as a gritty, fused precipitate in the form of its sodium compound, having the composition C=59.38 per cent, H=4.77 per cent, and Na=6.72 per cent. Experiments had shown that about 0.7 per cent of methyl alcohol on the dry weight of the wood is produced during digestion by the hydrolysis of the methoxyl groups of the lignin. On the assumption that wood contains 28 per cent of lignin and 3.8 per cent of methoxyl, it is calculated that the lignin itself contains 13.6 per cent of methoxyl, equivalent to 3 methoxyl groups in the molecule of lignin; thus 0.7 per cent of methyl alcohol represents half a molecule of methoxyl split off during the digestion. Assuming further that 2OH groups have become 2ONa, the lignin molecule $C_{39}H_{40}O_{12}$ should have become converted into $C_{38.5}H_{37}O_{12}Na_2$, the calculated percentage of sodium in which would be 6.2, as against 6.72 per cent found as above.

A further quantity of lignin was precipitated in the free state by treating the liquors with sulphuric acid after separation of the first precipitate. This first precipitate was also treated with acid to liberate the lignin and was purified by extraction with chloroform, whereby fatty and resinous acids were removed. The purified free lignin had the composition C=63.31 and H=5.24 per cent and yielded 12 per cent of methoxyl. From the filtrate there were obtained on distillation the volatile acids, formic and acetic, in fairly equal proportions. The residue after distillation contained lactones and lactonic acids, which were separated from the salts by treatment with alcohol and ether. The results obtained by the titration of these bodies corresponded well with the assumption that they are composed almost exclusively of saccharins and saccharinic acids with 6 carbon atoms.

Calculated on 1,000 Gm. of dry organic matter in the waste lyes, the results are summed up as follows:

	Grammes.
Lignin	542.9
Fatty and resin acids.....	24.7
Formic acid	36.9
Acetic acid	51.6
Lactones and lactonic acids.....	303.4
Total	959.5

Roughly speaking, these bodies may be taken as representing about 50 per cent of the dry substance of the wood, since relatively high yields of cellulose were obtained.

According to Klason, the formic and acetic acids are probably derived from the pentosans of the wood gum,

whilst the lactones and lactonic acids would be produced by the action of the alkali upon the readily hydrolysed hexose carbohydrates.

Working independently of Klason, Rinman (*Papierfabrikant*, 1912, 10, 39 and 101) has arrived at somewhat similar results, if account be taken of the different conditions of investigation. Rinman digested the wood with a mixture of sodium hydroxide and sodium chloride, obtaining an average yield of only 37 per cent of cellulose; the waste liquors would therefore contain a higher proportion of products derived from the decomposition of the cellulose than in Klason's experiments. The fraction described by Klason as "lignin" is termed "humus" by Rinman, who distinguishes those bodies precipitated by carbon dioxide by the name of "humus matters," whilst those precipitated by mineral acids are termed "humus acids." The sum of these two fractions always remains fairly constant, and they are apparently both derived from the same constituent of the wood, but their relative proportions vary with the conditions of digestion. Rinman states that the humus matter is not precipitated in the form of its sodium compound by treatment with carbon dioxide.

A further fraction, termed "soluble humus acids," may be precipitated as lead salts and liberated by sulphuretted hydrogen. One of the most interesting fractions of the liquors is that containing the lactonic acids; these acids are combined in the lyes with 40 per cent of Na_2O , and certainly contain a considerable proportion of ordinary lactic acid which has been isolated and characterized.

The major portion of Rinman's work is devoted to the industrial side of the question, and he has developed a new process of digestion, substituting sodium chloride for sodium sulphide and thus eliminating the mercaptan nuisance. A new method of regenerating the soda by a wet process analogous to the ammonia-soda process has been investigated, also a process for obtaining the acetic and formic acids. The most successful outcome of Rinman's work is the recovery of valuable by-products, spirits, ketones, oils and charcoal by the destructive distillation of the organic matters separated from the lyes.

American Minister Elliott Northcott, of Caracas, advises that Venezuela has adopted the metric as the official system of weights and measures, and has made its use obligatory in the courts and other public offices. An exception is made in the case of documents originating in a foreign county, where the money, weight, or measure of the country of origin may be expressed.

The Government of Madras Presidency, India, has approved of a proposal for the erection at Singanallur of a small central plant for crushing sugar cane and making jaggery, as an experimental measure during the present sugar-cane season, at an estimated cost of \$32,500. The Government also sanctions the local purchase of the outfit required for the experiment.

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NOTES AND COMMENTS.

The Cellulose Industry of Germany.

Examples of what the Germans have accomplished in the application of science to the utilization of waste are given in a series of articles on European industrial conditions, published in the *Scientific American*. The following relating to the manufacture of cellulose compounds from waste wood appears in the issue for June 22, 1912.

From Germany we can learn how to make the most out of a tree in an industrial way; for in Germany a tree which as a cord of wood is worth little more than three-fourths of a cent to a cent a pound, is converted into artificial silk worth \$2 a pound, and into artificial bristles of cellulose acetate worth \$4 a pound.

Thanks to the German chemist, trees may now serve to clothe a man. A whole industry has sprung up in the last decade for the express purpose of scientifically converting wood into cloth—wood, moreover, which would otherwise be wasted in fashioning round tree trunks into rectangular boards and beams. In Saxony, for example, a yarn called "xylolin" is made from paper as well as directly from wood pulp. From that paper, yarn, twine, cord, carpet, imitation canvas, and even whole suits of clothes have been made—all of them proof against the action of both hot and cold

water. A large corporation has built a factory not far from Berlin for the purpose of making "silvalin" yarn from spruce, of which there are fairly large tracts in Germany. Like its cousin "xylolin," "silvalin" can be woven in the loom to produce whole pieces of cloth which in their essence are nothing but transformed trees.

The whole German cellulose and nitrocellulose industry is a brilliant example of what efficiency means in the utilization of wood. The production of artificial silk from wood is alone a triumph of the application of science to industry. The credit for the original discovery belongs to Chardonnet. The process that he devised has not been very radically changed to this day. An ether-alcohol solution of nitrocellulose is employed. At first the liquid was squirted through a fine opening, the resulting thread congealing in cold water. Each thread was composed of a tube with a liquid interior. As it emerged from the fine opening, it was rather coarse, but it was spun into a thin filament later. Nowadays very fine openings are used, as small as 8-800 of a millimeter.

In the last twenty years, Germany has built up a huge industry on cellulose derivatives. All of them cannot even be mentioned here. In the manufacture of incandescent mantles, both for coating the mantle to enable it to withstand the shock of handling, and in the production of mantles themselves by the ejection of filaments containing the thorium and cerium, to be afterward woven into mantles; in the production of pyroxylin for imitation leathers and the manufacture of continuous film (an improvement which has undoubtedly contributed more than any other discovery to the popularity of photography and especially of the moving picture)—in all these we find that cellulose is nowadays employed as a vital necessity. Little did Schoenbein dream that the gun cotton (nitrocellulose) which he had invented would find far greater application in the arts of peace than in the art of war. Thanks to his discovery many articles hitherto made from expensive natural products are now made chiefly from wood waste. Between five thousand and six thousand patents on nitrocellulose and its uses are now to be found on the records. Even the scientist has benefited by the wider application of cellulose.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill building, Washington, D. C.

1,025,131. Alloy. James W. Donnell, Evanston, Ill. Patented May 7, 1912.

1,025,217. Composition Containing Vulcanized Oil and Process of Manufacture. Edwin Taylor, Farmingdale, N. Y., assignor to Union Clay Products Company, New York, N. Y., a corporation of New Jersey. Patented May 7, 1912.

1,025,356. Process of Converting Wood Into Paper-Making Stock and By-Products. Bailey F. Williamson, Gainesville, Fla. Patented May 7, 1912.

1,025,401. Process of Curing Hides. Frank P. James, Nashville, Tenn., assignor to The Electric Meat Cur-

ing Company, Cleveland, Ohio, a corporation of Maine. Patented May 7, 1912. The process consists in washing them to remove the surface accumulations, then immersing them in a solution of sodium chlorid, and passing an electric current through the solution and hides.

- 1,025,466. Method of Producing **Iron Albuminates** of Organo-mineral Acids. Paul Hoering, Berlin, and Otto Kippe, Osnabruck, Germany. Patented May 7, 1912.
- 1,025,469. Tubular Metallized **Filament**. Matthew A. Hunter, Schenectady, N. Y., assignor to General Electric Company, a corporation of New York. Patented May 7, 1912.
- 1,025,619. Process of Manufacturing **Phosphoric-Acid Compounds**. Felix Giese, Zoppot, and Wilhelm Wolters, Ildehausen, Germany. Patented May 7, 1912.
- 1,025,622. Treatment of **Sewage-Sludge**. Jacob Grossman, Manchester, England. Patented May 7, 1912.
- 1,025,628. Process of Treating **Wood**. John Warren Illingworth, Dorsey, Md. Patented May 7, 1912. The process consists in soaking it in water at ordinary temperature, then drying same, then sawing into planks, then soaking it in a saturated solution of lime water, then removing from said water and covering same with dry unslaked lime.
- 1,025,731. Process for **Waterproofing Linen** or Other Textile Articles and Giving Them a Permanent Glazed Washable Surface. Arthur Alphons Anthony Zimmer, London, England. Patented May 7, 1912.
- 1,025,760. **Electroplating** Process. Francis J. McElhone, Jersey City, N. J. Patented May 7, 1912.
- 1,025,945. **Polishing**. Peter Fireman, Washington, D. C., assignor to Magnetic Pigment Company, New York, N. Y., a corporation of New York. Patented May 7, 1912. This is a polishing agent, consisting of a suitable vehicle, and an abrading material whose principal constituent is precipitated magnetic ferro-ferric oxid.
- 1,025,948. Stable **Hydrogen-Peroxid** Solution. Otto Liebknecht, Frankfort-on-the-Main, Germany, assignor to Roessler and Hasslacher Chemical Co., New York, N. Y., a corporation of New York. Patented May 7, 1912.
- 1,025,956. Process For Obtaining **Refined Lead**. Julius Asbeck, Krantscheid-Westerwald, Germany. Patented May 14, 1912.
- 1,026,000. Process of **Degumming Silk**. Emil Schurrenberger, Paterson, N. J., assignor to Weidmann Silk Dyeing Co., Paterson, N. J., a corporation of New Jersey. Patented May 14, 1912.
- 1,026,094. **Arseno Compounds** and Process of Making Same. Robert Kahn, Frankfort-on-the-Main, Germany, assignor to Farbwerke vorm. Meister Lucius & Bruning, Höchst-on-the-Main, Germany, a corporation of Germany. Patented May 14, 1912.
- 1,026,156. **Hydrogenating Fatty Materials**. Carleton Ellis, Montclair, N. J., assignor to New Jersey Testing Laboratories, a corporation of New Jersey. Patented May 14, 1912.
- 1,026,361. **Insecticide**. Wilmon Newell, College Station, Texas. Patented May 14, 1912. The insecticide consists of arsenate of lead existing in the physical state of an impalpable powder.

C. L. PARKER

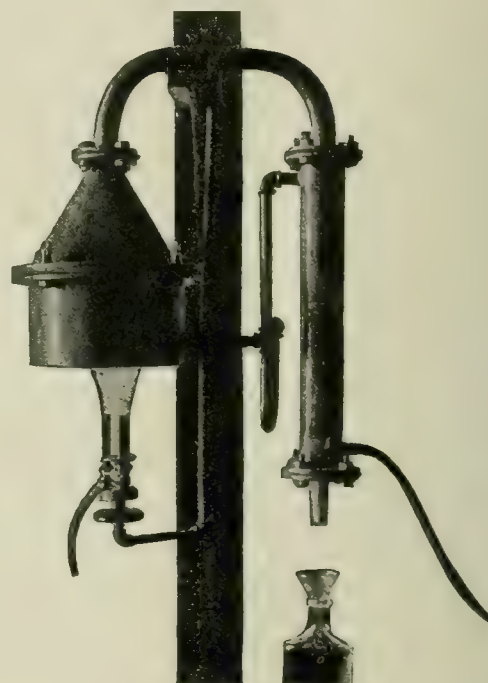
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THE WORK OF A MUNICIPAL GAS TESTING STATION.

By EDWARD K. HAMMOND.

A municipal gas testing station is maintained for the purpose of ascertaining the quality of the gas supplied to the city, and the chemist who carries on its work is interested only in the characteristics of the gas coming from the mains. The methods of manufacture used by the gas company are immaterial to him, provided the gas has the number of light and heat units required by the ordinance of his city and is properly freed from noxious impurities.

Municipal gas testing represents one of the most recent uses which have been found for applied chemistry. The work is essentially the same as that conducted in the laboratory of a gas company, but the greatest stress is laid upon those tests which show the ultimate value of the gas to the consumer. This makes calorimetric and photometric determinations, a survey of the pressure conditions throughout the city, and tests to determine whether the gas has been freed from such objectionable impurities as sulphur and ammonia the points of vital importance. Volumetric analysis is a minor consideration. The value of the data secured from this source lies in the opportunity which it presents to form an opinion of the service in outlying districts by bringing samples of gas in to the laboratory for analysis.

The discussion of the practice of an up-to-date municipal gas testing station presented in this article may, however, be taken as a reliable guide for either municipal or corporation service, as the methods outlined are perfectly general in their application and represent the most advanced ideas on the subject.

With the exception of volumetric analysis, the results of all gas tests are based upon a metered volume and, as this volume varies with changes in temperature and pressure, in accordance with the laws of Charles and Boyle, it was found necessary to adopt a standard of reference which would make it possible to compare the results of different chemists. This standard has been arbitrarily fixed at a temperature of 60° F. and an absolute pressure of 30 ins. of mercury.

PHOTOMETRIC TESTS.

In testing the illumination produced by a gas flame, the results are expressed in the familiar unit known

as the candle power, which is defined as the light emitted from an English sperm candle when burning at the rate of twenty grains in ten minutes. The light produced by such candles is also the ultimate standard against which the illumination of the gas is compared, but for the sake of convenience, and also to reduce the expense involved, the candles are replaced by a standard known as the Harcourt pentane lamp, which is used for routine work in most gas laboratories. A lamp of this type is designed to give ten candle power, but this value is subject to fluctuations, caused by vari-

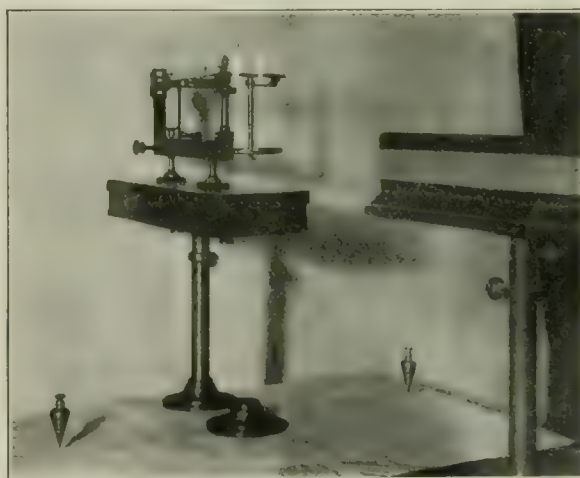


Fig. 1—Candle Balance.

ations in the pentane used, by atmospheric conditions and by other causes. Consequently, the light emitted by the pentane lamp should be compared with that of the sperm candles, at intervals of about a month, in order to obtain its true value. Thus the sperm candles are the ultimate standard against which the illumination of the gas is compared.

In calibrating the pentane lamp against candles, a balance is used which carries two candles in clips at one end of the beam. Such a candle balance is illustrated in Fig. 1, which provides for burning a fixed amount of sperm during the course of the test. Before starting to make observations, both the candles and the pentane lamp are allowed to burn for about fifteen minutes, in order to secure constant conditions during the test. For a few minutes after lighting, the rate of combustion varies considerably and this causes a corresponding variation in the amount of light which is emitted.

The room used for making photometric tests must be completely darkened, and to cut off reflected light from the flames in the room the walls are painted dead black. In order to keep the atmosphere clear, an electric exhaust fan is used, which draws in fresh air through ventilators situated near the floor and discharges it into vents connecting with ducts between the double ceiling. The equipment of this room consists of a long table, upon opposite ends of which stand the pentane lamp and the candle balance. Extending between these two sources of light there is a graduated bar upon which the sight box is mounted upon a movable base. This sight box is fitted with a waxed paper disc, upon which the light from the two sources at the opposite ends of the table is received, and by adjusting the position of this sight box along the bar until the illumination at either side of the disc is the same, the light emitted by the source under test is read directly on the graduated bar. Figs. 1 and 2 show the two ends of the table arranged for conducting a calibration of the pentane lamp against sperm candles. As the intensity of the illumination from any source varies inversely as the square of the distance from the source, it is of the greatest importance to have the pentane lamp and the candles properly set in relation to the bar. This is provided for by the plumb lines shown in the illustration. The points of the weights hang over lines marked on the table. The candle flames are then lined up with the plumb lines, while in the case of the pentane lamp, the plumb line attached to the lamp is brought into alignment with the two lines hanging over the table.

In preparing the candle balance for use, the rider on the beam is so set that the weight of the burning candles is just too heavy to counterpoise the weight of the beam. It is evident that as the candles burn down, they will become lighter, and when the point is reached where the balance is momentarily in equilibrium, the time of starting the test is recorded with a stop watch. Weights are then placed in the pan beneath the candles—the amount depending upon the duration of the test which is to be made—and a series of readings are then taken at intervals of one minute. For all ordinary purposes, a fifteen minute test is sufficient, and as the rate at which the candles burn is approximately twenty grains in ten minutes, it is evident that sixty grains in weights must be placed in the balance pan to replace the amount of sperm that will be consumed from two candles during the fifteen minute test. After taking the seventh reading, the photometer sight box is reversed about the pivot on which it is mounted, so that the opposite sides are exposed to the respective ends of the table. This is an important point in all photometric work, because a considerable difference is frequently found in the readings after the disc has been reversed. By reversing the sight box, however, any inequalities in the readings of opposite sides of the disc is compensated for.

In most cases, the illumination value of the pentane lamp, and also that of the gas which is tested against it, is expressed in terms of the light emitted under actual room conditions. Consequently, the affect of atmospheric conditions is disregarded. The method of making calculations for a typical set of figures for a calibration test of fifteen minutes' duration is shown below.

Reading No.	
1	4.95
2	4.97
3	4.92
4	4.90
5	4.96
6	4.98
7	4.99
8 (disc reversed)	4.93
9	4.95
10	4.98
11	4.92
12	4.94
13	4.94
14	4.98
15	4.90

Average value 4.947

As two candles were used for the test, the average value must be multiplied by two, thus giving 2×4.947

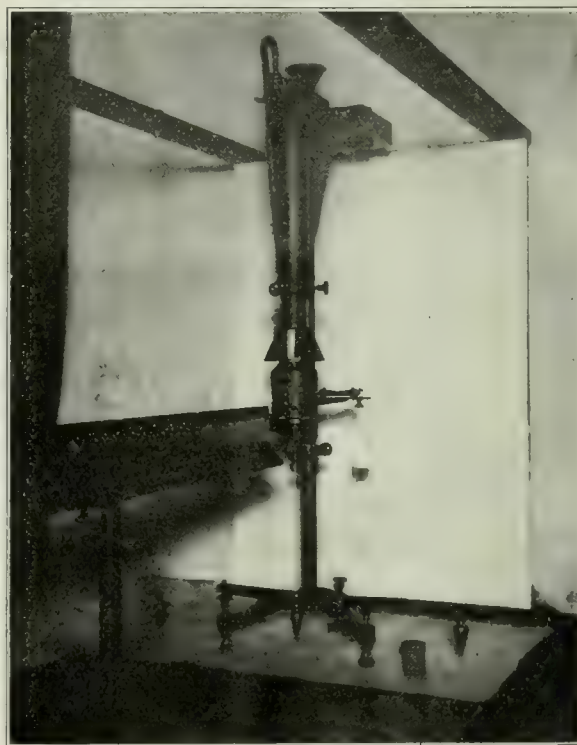


Fig. 2.

= 9.894 candle power as the uncorrected value of the pentane lamp.

The time required to burn sixty grains of sperm from the candles was 15 minutes, 16.8 seconds, or 916.8 seconds, as determined with the stop watch. The light which the candles are emitting is thus less than the theoretical two candle power, their true value being 900.0

— of the theoretical. As a consequence, the observed value of the pentane lamp must be multiplied by this ratio to correct for the discrepancy in the rate

at which the candles are burning. It will, of course, be evident to the reader that if the candles were burning too fast, instead of too slow, the light emitted by them would be above the theoretical candle power. This would make the observed value of the pentane lamp below its true value and the correction factor applied would be greater than unity.

For the calibration previously outlined, the average observed value for the lamp was 9.894 candle power. Multiplying this value by the correction factor gives

$$9.894 \times \frac{900.0}{916.8} = 9.721 \text{ candle power as the corrected}$$

value of the pentane lamp for existing atmospheric conditions.

If the light emitted by the pentane lamp is compared with an electric standard, which is not subject to variations caused by the affect of atmospheric conditions, then the readings of the photometer represent the actual light that the lamp is giving at the time of the test. This value can then be corrected for the affect of humidity and barometric pressure upon the illumination produced by the pentane lamp. For this correction, the wet and dry bulb thermometers are used to determine the humidity. The manufacturers of the standard forms of wet and dry bulb thermometers have compiled tables, which are an abridge arrangement of the results of researches by C. F. Marvin, professor of meteorology, under the direction of Willis L. Moore, chief of the United States Weather Bureau. These tables provide a rapid and accurate method of determining the dew point, the relative humidity and the vapor pressure from the observed difference in the readings of the wet and dry bulb thermometers.

For use in making a sample calculation, it will be assumed:

1. That the value of the pentane lamp, as secured by a photometric test against an electric standard, is 9.45 candle power.

2. That the readings of the dry and wet bulb thermometers were 82 and 71, respectively, which gives $82 - 71 = 11^\circ \text{ F.}$ as the depression at the wet bulb, due to the loss of heat caused by the evaporation of sufficient water to bring the surrounding atmosphere to the saturation point.

3. That the reading of the barometer was 29.18 ins. at the time the test was made.

Reference to the dew point tables gives 66° F. as the dew point and 0.091 ins. of mercury as the vapor pressure at the time the lamp was calibrated. The next step is to secure the actual pressure of the dry air, which is done by subtracting the vapor pressure from the barometer reading. This gives $29.18 - 0.091 = 29.089$ ins. of mercury. The amount of aqueous vapor present in the atmosphere is now calculated as the percentage of water vapor per cubic meter of dry air. Calling the barometric pressure B and the

E

vapor pressure E; $\frac{E}{B-E}$ represents the per cent of

water vapor in the air. By substituting known values

$$\text{for E and B we get, } \frac{0.091}{29.180 - 0.091} = \frac{0.091}{29.089} =$$

0.003128. Multiplying this result by 1,000 gives 3.128 per cent as the quantity of water vapor per cubic meter of dry air.

With the view of enabling the work of different investigators to be compared, or to allow a chemist to compare the results of his determinations on different days, when atmospheric conditions will have changed, a humidity of 8.0 per cent of water vapor per cubic meter of dry air, and a barometric pressure of 29.92 ins. of mercury have been adopted for a standard. The results of experiments show that for each additional 1.0 per cent of water vapor present in the atmosphere in which a pentane lamp is being burned, the light actually emitted is reduced 0.57 per cent. Also, each decrease of 1.0 in. of mercury in the barometric pressure decreases the amount of light emitted by the lamp 1.5 per cent.

The necessary data are now available for correcting the photometric test of the pentane lamp against the electric standard for the effect of the humidity and pressure of the atmosphere. The result expresses the value of the lamp under the standard conditions of pressure and humidity and is known as the standard value of the lamp. The method of making the calculation is shown below.

Subtracting the barometric pressure from the standard of 29.92 ins. of mercury gives $29.92 - 29.18 = 0.74$ ins. of mercury as the amount that the pressure is below standard. Bearing in mind that each one inch increase in the pressure causes an increase of 1.5 per cent in the light actually emitted by the pentane lamp, the necessary correction for 0.74 ins. must be added to the observed value of the lamp. Subtracting the existing humidity of 3.128 per cent from the standard value of 8.0 per cent gives $8.000 - 3.128 = 4.872$ per cent as the amount that the existing humidity conditions at the time of the test are below standard. Remembering that each 1.0 per cent of water vapor below the standard 8.0 per cent increases the light actually emitted by the lamp by 0.57 per cent, the necessary correction for this lack of humidity must be added to the observed value.

Calling S the standard value of the lamp, the corrections for atmospheric conditions are substituted in the following equation, which is then solved for the required value of the lamp under standard conditions.

Standard value = value obtained by comparison + algebraic sum of the corrections.

$$S = 9.45 + 0.74 \times 0.015 \times S + 3.128 \times 0.0057 \times S$$

$$S = 9.45 + 0.0111 \times S + 0.0178 \times S$$

$$0.9711 \times S = 9.45$$

$$S = \frac{9.45}{0.9711} = 9.73 \text{ candle power.}$$

It will be evident from the above calculation that the algebraic signs of either of the corrections will

be reversed if the humidity or the barometric pressure is on the opposite side of the arbitrary standard of 8.0 per cent water vapor and 29.92 ins. of mercury pressure from the conditions existing at the time the above test was made. By the same method of calculation, the actual amount of light emitted from any exposed source under existing atmospheric conditions may be calculated if its value under standard conditions has been found.

The results of these calculations for reducing photometric determinations to standard or actual figures emphasizes the advantages of an electric standard as an ultimate reference over the sperm candles commonly used. The electric standard enables results to be obtained which have an absolute value while those secured with candles are merely relative. An electric standard is also more simple to operate than either the candles or the pentane lamp and the time will doubtless come when electric standards will be universally used for photometric determinations. It is merely a matter of the time required to work away from the traditional use of candles.

In a well organized gas testing laboratory, the manufacturer's calibration of equipment should never be accepted without verifying its accuracy by actual experiment. Consequently, after completing the calibration of the pentane lamp, it still remains to determine the accuracy of the meter and its thermometers, which are used to determine the volume and the temperature of the gas burned during the course of a test, before things are in readiness to make a photometric test of the gas supply.

For testing the meters used in a gas laboratory, a more accurate form of apparatus is required than the type which is used for proving the meters placed on the consumers' service pipes. A good form of laboratory prover is illustrated in Fig. 3, which holds exactly 1 cu. ft. of gas between the indices I_1 and I_2 . In using this prover, water at room temperature is allowed to flow in from a reservoir connected with the water valve until its level has reached the upper index I_1 . The lower valve is then closed and the reservoir is lowered below the level of the prover. The gas valve is now opened, after which the water valve is opened for a sufficient length of time to allow the water level to drop to the lower index I_2 . The readings of the thermometers T_1 and T_2 are now noted, and if they are found to be the same, it indicates that the conditions are right for proving the meter. If, on the other hand, there is any material difference in these temperatures, it will cause a change in the volume of gas, during the test, and this will viciate the accuracy of the meter calibration. The correct relation between the temperatures T_1 and T_2 is obtained by adding hot or cold water to the contents of the reservoir, from which the prover is filled, until the readings of the thermometers coincide. When this condition has been secured, the gas valve is connected with the inlet of the meter by means of a piece of

rubber tubing. The water reservoir is then raised to its former height above the prover and the water valve is next opened sufficiently to allow the water to rise slowly in the prover. The progress of the water during this part of the test can be observed by watching the rising level in the gauge glass which has been provided for the purpose. Toward the end of the run the flow through the water valve is shut down to a very small amount, in order that it may be instantly stopped when the water reaches the upper index I_1 . When this point is reached, it means that exactly 1 cu.

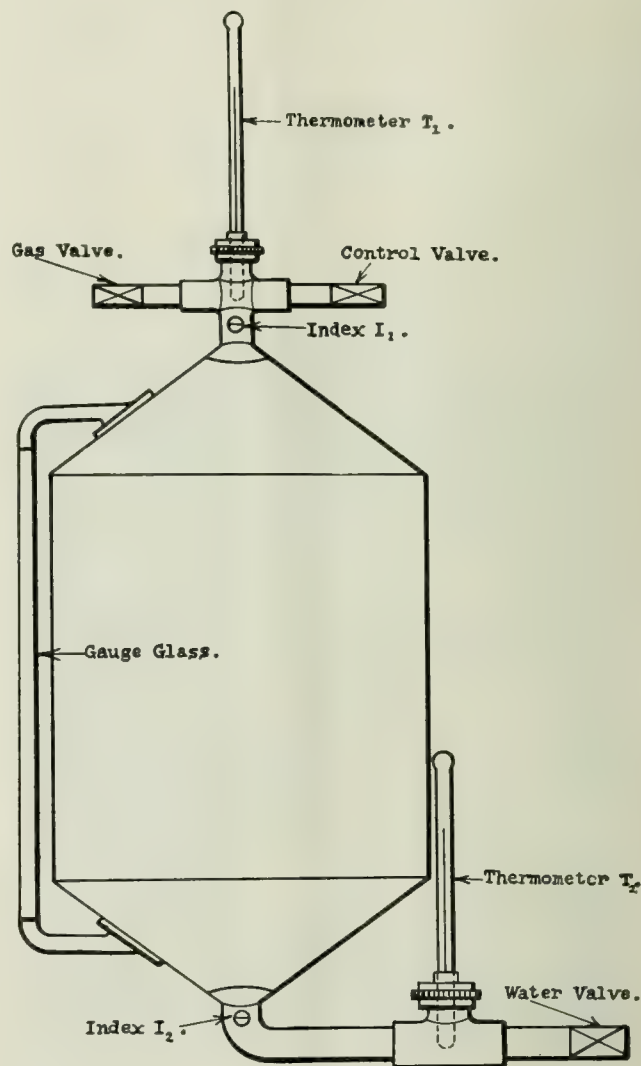


Fig. 3—Laboratory Prover.

ft. of gas has been passed through the meter. Consequently, the difference between the first and last readings of the meter dial should be 1.000 cu. ft. if the meter is accurate. Any slight deviation from the correct reading can be compensated for by applying the necessary correction factor to the volumes registered by the meter. If, however, any serious discrepancy should be exposed by the prover, the meter should be rejected and returned to the manufacturers.

All thermometers which have not been tested by the Bureau of Standards should be calibrated before accepting their readings for use in making gas labora-

tory determinations. Such calibrations are easily conducted by suspending the thermometer to be tested in a beaker of water with one whose readings are attested to by a Bureau of Standards certificate. The test is started with the temperature of the water considerably below the range to be covered in making laboratory determinations. The temperature of the water is then raised, a little at a time, by adding hot water to the contents of the beaker. Both thermometers are read at each step in the test and a table is prepared showing the corrections which must be made on different readings of the thermometer which is being tested. This table should then be reproduced on a tag and attached to the thermometer, so that it is always at hand for use in correcting the readings of the thermometer when it is in use.

To be continued.

LIST OF NEW PUBLICATIONS OF THE BUREAU OF MINES.

The following is the June, 1912, list of new publications of the Bureau of Mines, United States Department of the Interior:

Bulletin 41—Government coal purchases under specifications, with analyses for the fiscal year 1909-10, by G. S. Pope, with a chapter on the fuel-inspection laboratory of the Bureau of Mines, by J. D. Davis. 1912. 99 pp. 3 pls.

Technical Paper 5—The constituents of coal soluble in phenol, by J. C. W. Frazer and E. J. Hoffman. 1912. 20 pp.

Technical Paper 9—The status of the gas producer and of the internal-combustion engine in the utilization of fuels, by R. H. Fernald. 1912. 42 pp.

Technical Paper 19—The factor of safety in mine electrical installations, by H. H. Clark. 1912. 14 pp.

Technical Paper 20—The slagging type of gas producer, with a brief report of preliminary tests, by C. D. Smith. 1912. 14 pp.

Reprint of Bulletin 39—The smoke problem at boiler plants, a preliminary report, by D. T. Randall. 31 pp. Reprint of United States Geological Survey Bulletin 334, revised by S. B. Flagg.

The Bureau of Mines has copies of these publications for free distribution, but can not give more than one copy of the same bulletin to one person. Requests for all papers can not be granted without satisfactory reason. In asking for publications please order them by number and title. Applications should be addressed to the Director of the Bureau of Mines, Washington, D. C.

The amalgamation of Scottish bar iron manufactures has just been made under the style of the Scottish Iron & Steel Co. (Ltd.), share capital \$3,650,000, and debentures \$1,460,000. The company embraces 13 companies operating 15 works having a combined output of 250,000 tons per annum.

THE LIQUID PURIFICATION OF ILLUMINATING GAS.*

By CLARENCE A. SCHNERR.

During recent years, improvements in the purification of illuminating gas have been the subject of keen research and of lengthy discussions for many obvious reasons. Dissatisfaction with the use of iron oxide, coupled with a lowering of gas rates as well as powerful electric competition, has compelled the gas engineer to carefully economize in all parts of the manufacture and distribution of his product. It may be asserted and with perfect truth that following the general policy, improvements have been made on the present purifying system, but probably no gas man is willing to express his perfect satisfaction with the present purification; indeed the general discontent has manifested itself in a constant search for something better. This paper is primarily designed to show the development of a new process and for this purpose ample details will be given.

Purification may be carried on by means of three agents: Solid, liquid or gaseous, or by any combination of the three. Before 1905, practically all elimination of the hydrogen sulfur was effected by means of solid purifying materials. Lime first attained prominence in this direction and proved to be such a nuisance that it was finally discarded in the progressive plants. Iron oxide in various forms was then substituted, oxidized borings, bog ore and even precipitated ferric hydrate found favor at various plants. These materials are in use in practically all the gas works of the world at the present time.

Weldon mud (manganese dioxide) and various prepared mixtures were used, but usually with the same result; they all removed hydrogen sulfide, but the use and handling of large masses of solids was entirely unsatisfactory.

Research on purification then turned to some purifying material more easily handled and of greater economic value; by this we mean cheapness of material and principally the recovery of the great by-product of hydrogen sulfide extraction—sulfur.

Several years ago Walther Feld, a prominent German gas man, became actively engaged on a process which he later covered with international patents, and pushed to a successful conclusion. It is being used in England and the United States for the purification of both coal and water gas.

The Feld Liquid Purification System.—As originally intended, only the hydrogen sulfide was to have been eliminated, but it was improved later so that it now removes the ammonia and the hydrogen sulfide simultaneously, the active reagents being the sulfate, thiosulfate and thionate of iron. Other salts of a similar nature may be used. The hydrogen sulfide forms an additive compound with the iron salts, which is then

*Abstract of paper read before the Eighth Annual Meeting of the Illinois Gas Association, March 20, 1912.

broken up by means of sulfur dioxide, forming S and water; the liquor being used repeatedly.

The gas is first scrubbed in a Feld centrifugal washer with a weak solution of ferrous sulfate, ammonium sulfate being formed and ferrous sulfide precipitating. The liquor from the washer is then treated with sulfur dioxide obtained by burning sulfur in an excess of air. Upon contact, free sulfur is precipitated, and soluble ferrous sulfate, thiosulfate and thionate formed. The liquor so regenerated is again used for treating the crude gas, but on account of the thionate and thiosulfate in the liquor, only that portion of hydrogen sulfide corresponding to the ammonia, or about one-half of the total hydrogen sulfide, is eliminated.

The liquor is treated alternately with crude gas and sulfur dioxide until it contains from 30% to 45% of ammonium salts. It is then ready for the oxidation necessary to convert the thionates and thiosulfates into sulfates. This step is necessary because a large part of the ammonia content is in the form of sulfite, and is not in the most available commercial form. For this reason the hot liquor is treated with sulfur dioxide and an excess of air, after which it contains from 30% to 45% of ammonium sulfate, the original amount of ferrous sulfate in solution, and all the sulfur extracted from the gas in the form of free, precipitated sulfur. The sulfur is separated by filter pressing, and enough is burned to furnish sulfur dioxide, the remainder being for sale.

The liquor in the filter press is treated with the crude gas, the ammonia and the hydrogen sulfide content decompose the ferrous sulfate, forming insoluble ferrous sulfide and soluble ammonium sulfate. The ferrous sulfide is separated by filter pressing, and the liquor consists of a pure and concentrated solution of ammonium sulfate, which is obtained by evaporation.

The residue in the filter press, consisting of ferrous sulfide with some inherent ammonium sulfate liquor, is mixed with fresh liquor and treated with sulfur dioxide. Soluble ferrous thionate, thiosulfate and sulfate are formed and are used again for the extraction of ammonia and hydrogen sulfide.

Now this process is deeply technical, and requires constantly skilled supervision and attention. Several points selected at random will serve to illustrate this: Frequent gassing with sulfur dioxide is required, and this is not merely a haphazard addition of the gas, but a very precise operation, with frequent testing to determine the proper amounts. Again the oxidation of the sulfite to sulfate is an operation which the unskilled workman cannot perform. However, this method shows many desirable features.

Ammonia; the extraction is independent of temperature; a continued use of the same liquor is possible; ammonia is easily secured from a saturated solution as ammonium sulfate; no distillation required to secure the ammonia; the use of sulfuric acid is avoided; hydrogen sulfide; from 50 per cent to 80 per cent of the total hydrogen sulfide is extracted

simultaneously with the ammonia; after first washing liquors have been formed, no chemicals are required; sulphur is obtained as a by-product and is commercially saleable; apparatus; the plant is not complicated, and since it requires very little space, may be put in any ordinary building; power and steam are low.

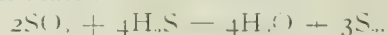
This is then the perfected Feld process for coal gas purification. Laboratory practice has shown its efficiency on a small scale, but owing to the recency of its installation on a plant basis, it has not been thoroughly tried out on a large plan. It is true that two plants are making use of this system, but it is still, without a doubt, in the experimental stage.

The application of the Feld process to the removal of hydrogen sulfide only has been made at the East Hull gas works, England, and since it is in continued use, we may infer that it has at least partially fulfilled the claims made for it.

The primary object in the East Hull installation was the complete removal of hydrogen sulfide and the subsequent recovery of free sulfur.

A Proposed Liquid Purification for Water Gas.—Practically all of the systems developed are mainly for use in coal gas practice. However, since a vast amount of the American gas industry is based on the water gas type, the problem of working out some simple process which was especially adapted to water gas became very interesting.

Hence, research has been carried on to discover some efficient liquid purifying agent for water gas. The process as developed is based on that ancient and well known reaction:



Whenever sulfur dioxide and hydrogen sulfide meet in aqueous solution or in the presence of moisture they react to form water and free precipitated sulfur.

1. The absorption of the hydrogen sulfide from the gas.

2. The recovery of sulfur as a by-product.

The method in brief is operated as follows: A solution of sulfurous acid or more properly sulfur dioxide, dissolved in water, is used to scrub the gas in towers or washers of any type with one object, perfect contact between the gas and the liquor. As the contact is secured, the primary reaction takes place and we have free sulfur and water as resultant products.

The required sulfur dioxide is supplied by a small burner with fan attachment. This gas is then passed into a small washer or simply an agitated vat for absorption by the gas saturated water. It is then drawn into the washers as needed. As the liquor becomes exhausted, it is again saturated with sulfur dioxide to any desired strength and is again used in the washers. The same solution can therefore be used indefinitely or until limited by the cleanliness or volume of the liquor. This eliminates any necessity for constantly saturating with gas the liquor passing through the washers.

The precipitated sulfur may be carried in the solution until it forms about 15 per cent by weight and is then removed by filter pressing. A portion of this sulfur is used in the sulfur burner and the remainder sold. According to the theory, one-third of the sulfur must be reused on each operation, but it is readily apparent that after the first acid solution is prepared all the sulfur extracted from the gas is for sale, because the acid solution is carrying practically the same sulfur content until it is finally exhausted and ready to be run into the sewer.

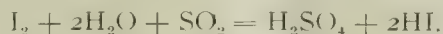
The Experimental Work.—For the experimental work a gas line was carried from the outlet of the shaving scrubbers to the laboratory. In this way crude gas was obtained for the apparatus under the same conditions existing in the present purifiers.

The washing apparatus, although very simple, deserves mention. A large glass tube, and at times a duplicate, $2\frac{3}{8}$ by 22 ins., was filled with 60 $\frac{1}{4}$ -in. tubes supported in such a manner that the gas and the washing liquor passed both inside and outside them. This arrangement probably gives as large a surface as can possibly be obtained and at the same time have an apparatus that will automatically pass all precipitated sulfur out the flush pipe. The checkered scrubber is not to be considered for this reason: Any sulfur precipitating in the brick work tends to impede the flow of gas, even heavy flushing failing to remove it.

The total absorption surface was 2,050 sq. in. Convenient cocks were left on either side of the apparatus so that samples of crude or clean gas could be easily obtained, pressures noted, etc.

Now, the first things for us to consider are the chemical checks on reagent, exhausted liquor, incoming and outgoing gas, the purity of the precipitated sulphur, etc.

Determination of the Sulfur Dioxide Content of the Wash Liquor.—The method proposed by F. Reich (Chem. Zeitung, 1858) and later described by Cl. Winkler in his *Anleitung zur Untersuchung der Industrie Gase*, Part II, pages 118, 353, appears very promising. The basic reaction is:



Iodine oxidizes the sulfur dioxide to sulfur trioxide by forming hydriodic acid. This reaction is reversible if more than .04 per cent sulfur dioxide is present in the solution, according to Hempel, but later authorities assert that if the sulfur dioxide is run into the starch bearing iodine instead of running the iodine starch into the dioxide solution, the reaction is not reversible even for strong solutions. The latter iodimetric method was found by experiment to be sufficiently accurate to serve as a check on all wash liquors.

Checking the Purity of Outgoing Gas.—The Tutwiler as used at present could be used to show any hydrogen sulfide escaping with the gas and would also show sulfur dioxide blowing from an excessively

saturated solution, but any dioxide present in the outgoing gas would cause the readings to be abnormally low. It seems best then to use the silver nitrate stain, which will show any traces of hydrogen sulfide escaping and then use the Tutwiler. Any reading of the latter should be multiplied by four, if no trace of hydrogen sulfide is present. In case both are present in any quantities, the Referee's Test for total sulfur seems at present the only really accurate method to use. The gas entering the washers is checked with the Tutwiler for the hydrogen sulfide content.

Tests on the By-Product Sulphur.—In the crude gas at our disposal, the tar content varied and seemed to depend somewhat on the condition of the shaving scrubbers, but for the most part was simply the tar mist coming through all dry scrubbers. The wash liquors darkened slightly and nearly all the condensed tar came with the sulfur. This problem may be solved by the use of the hot tar spray washers or scrubbers. Thus the quality of the sulphur should be improved.

The average purity of the sulfur as found, 97.785 per cent, does not meet the requirements of the powder and other industries using a 99.5 per cent refined sulfur, but it would form an admirable agent for bleaching, insecticide and acid making, etc. Hence it would be used by the textile, agricultural, paper, syrup and acid industries. In time we are convinced that all the sulfur turned out of the gas plants will be refined because the necessity is certain to show a cheap method of refining. But at the present time the grade of sulfur produced can be disposed of at a fair price for the crude product.

Operation of the Experimental Apparatus.—We now turn to the actual purification and note the influence of various agencies: Temperature, varying sulfur dioxide saturation, etc., on the process. In nearly every instance the duration of each test was two hours. Variations in temperature were easily secured since the testing began in the summer and continued until mid-winter. The gas rate per hour, square feet, etc., are all given on a corrected basis.

The following tables show just how the purification was affected by keeping as nearly as possible all conditions exactly similar, with the one exception mentioned in each case. For example: In Table A

TABLE A.						
No.	Liters, solution per 24 hrs.	Per sq. ft.	Cu. ft. gas per 24 hrs.	Per sq. ft.	Grams SO ₂ per liter.	Temp. solution, F°.
1.	172.80	12.2	22.800	1.61	.78142	64
2.	175.20	12.3	22.728	1.61	.86200	64
3.	174.75	12.3	22.585	1.59	.81540	66
4.	175.00	12.3	22.600	1.60	2.60747	66
5.	176.05	12.4	22.550	1.59	7.46515	64
6.	174.80	12.3	22.580	1.59	14.74219	64
7.	175.15	12.3	22.745	1.61	19.65142	62
No.	Temp. F°.	H ₂ S grs. per 100 cu. ft. crude.	H ₂ S & SO ₂ in grs. per 100 cu. ft. purified.	Stain with lead acetate.		
1.	74	80	5 ..	None		
2.	75	85	4 ..	None		
3.	78	120	6 ..	Slight		
4.	77	110	3 ..	None		
5.	74	90	3 ..	None		
6.	74	90	.. 7	None		
7.	71	90	.. 14	None		

practically all conditions were similar for all the tests, excepting the sulfur dioxide content of the wash liquor, which was varied so as to show maximum and minimum limits. This then gives the most economical concentration for ordinary practice. The concentration of the dioxide ranged from .78442 to 19.65142 grams per liter of water. Theoretically about 75 grams of sulfur dioxide would represent a fully saturated solution. In the experimental work, as the table shows, the dioxide seems to be carried off by the gas after the saturation passes about 10 grams per liter. For example, in tests 6 and 7, no stains appeared even with silver nitrate on long exposure, but the Tutwiler gave an equivalent of 7 and 14 grains of sulfur dioxide respectively. This then seems to show conclusively that above a certain degree of saturation sulfur dioxide is given off by an agitation of the solution, and since it is as much of an objection as the hydrogen sulfide, that degree of saturation

must not be exceeded. This escape of the dioxide seems partially to be independent of the temperature to which the solution is subjected.

Table B illustrates a maximum and minimum amount of wash liquor per square foot of the washing surface per 24 hours from 12.2 to 3.5 liters. Notice the tests 3 and 4. In test 3 the amount of liquor per square foot per 24 hours was 8.4 liters with a hydrogen sulfide content of 3 grains in the purified gas; in test 4 with a reduction of only 2 liters per square foot per 24 hours, the sulfide content advances to 7 grains per cubic foot. This sharp contrast then shows two probable causes—insufficient covering of the washing surface or not enough dioxide to properly carry out the reaction. We have, however, theoretically a heavy excess of the reagent, and in proportion it has purified large amounts of gas per liter of solution, so we must conclude that this excess of hydrogen sulfide in the purified gas is simply due to

TABLE B.

No.	Solution per 24 hrs. Liters.	Per sq. ft.	Cu. ft. gas per 24 hrs.	Per sq. ft.	Grams SO ₂ per liter.	Temp. solution, F°.
1.	172.80	12.2	1421.50	100.10	9.81065	64
2.	150.00	10.5	1422.45	100.18	9.81070	63
3.	120.00	8.4	1420.15	100.01	9.81068	63
4.	90.45	6.4	1421.20	100.08	9.81068	64
5.	75.55	5.3	1422.10	100.18	9.81072	65
6.	60.06	4.2	1420.18	100.01	9.81074	64
7.	50.10	3.5	1422.15	100.17	9.81065	65

No.	Temp. F°.	H ₂ S grs. per 100 cu. ft. crude.	H ₂ S & SO ₂ in grs. per 100 cu. ft. purified.	Stain with lead acetate.
1.	74	80	3 ..	None
2.	76	80		None
3.	71	90		None
4.	68	85	7 ..	Stain
5.	72	85	9 ..	Stain
6.	72	85	9 ..	Stain
7.	72	85	15 ..	Stain

TABLE C.

No.	Varied gas rate. Liters. solution.	Per sq. ft.	Cu. ft. gas per 24 hrs.	Per sq. ft.	Gram SO ₂ per litre.	Temp. solution, F°.
1.	120.00	8.4	1420.20	100.00	9.81075	65
2.	120.00	8.4	1435.50	101.90	9.81070	65
3.	120.00	18.4	1440.45	1014.40	9.81074	65
4.	120.00	18.4	1425.50	1004.00	9.81071	65
5.	120.00	18.4	1440.60	1014.70	9.81070	65
6.	120.00	8.4	1200.40	84.54	9.81068	64
7.	120.00	8.4	900.42	63.41	9.81068	64
8.	120.00	8.4	700.50	49.33	9.81050	67
9.	120.00	8.4	515.60	36.31	9.81064	67
10.	120.00	8.4	320.15	22.55	9.81065	66
11.	120.00	8.4	180.96	12.74	9.81070	66
12.	120.00	8.4	156.00	10.95	9.81055	66
13.	120.00	8.4	73.80	5.20	9.81078	65
14.	120.00	8.4	48.36	3.40	9.81064	64
15.	120.00	8.4	20.64	1.45	9.81072	65

No.	Temp. F°.	H ₂ S grs. per 100 cu. ft. crude.	H ₂ S & SO ₂ in grs. per 100 cu. ft. purified.	Stain with lead acetate.
1.	65	90	2	None
2.	65	90	2	None
3.	66	90	6	Stain
4.	66	90	5	None
5.	65	90	6	Stain
6.	66	85	2	None
7.	66	85	2	None
8.	65	90	2	None
9.	64	90	..	None
10.	66	90	..	None
11.	66	85	..	None
12.	65	90	..	None
13.	64	90	..	None
14.	66	95	..	None
15.	66	90	..	None

TABLE D.

No.	Varied liquor rate. Liters. solution.	Per sq. ft.	Cu. ft. gas per 24 hrs.	Per sq. ft.	Gram SO ₂ per litre.	Temp. solution, F°.
1.	120.00	8.4	1420.00	100.00	9.81056	83
2.	120.00	8.4	1425.00	100.35	9.81070	74
3.	120.00	8.4	1423.15	100.22	9.81060	56
4.	120.00	8.4	1421.45	100.10	9.81074	40
5.	120.00	8.4	1422.54	100.18	9.81065	45

No.	Temp. F°.	H ₂ S grs. per 100 cu. ft. crude.	H ₂ S & SO ₂ in grs. per 100 cu. ft. purified.	Stain with lead acetate.
1.	88	105	2 ..	None
2.	86	100	2 ..	None
3.	87	100	2 ..	None
4.	85	110	2 ..	None
5.	86	105	2 ..	None

TABLE E.

No.	Varied gas temperature. Liters. solution.	Per sq. ft.	Cu. ft. gas per 24 hrs.	Per sq. ft.	Grams SO ₂ per litre.	Temp. solution, F°.
1.	120.00	8.4	1420.00	100.00	9.81076	60
2.	120.00	8.4	1425.00	100.35	9.81070	62
3.	120.00	8.4	1423.15	100.22	9.81075	66
4.	120.00	8.4	1418.15	99.87	9.81052	63
5.	120.00	8.4	1419.25	99.94	9.81064	62

No.	Temp. F°.	H ₂ S grs. per 100 cu. ft. crude.	H ₂ S & SO ₂ in grs. per 100 cu. ft. purified.	Stain with lead acetate.
1.	88	100	2 ..	None
2.	74	105	2 ..	None
3.	66	100	2 ..	None
4.	60	100	2 ..	None
5.	55	100	2 ..	None

TABLE F.

No.	Varied H ₂ S content in crude gas. Liters. solution.	Per sq. ft.	Cu. ft. gas per 24 hrs.	Per sq. ft.	Grams SO ₂ per litre.	Temp. solution, F°.
1.	120.00	8.4	1421.45	100.10	9.81066	65
2.	120.00	8.4	1423.60	100.25	9.81074	65
3.	120.00	8.4	1422.18	100.15	9.81077	64
4.	120.00	8.4	1421.15	100.08	9.81080	65
5.	120.00	8.4	1420.16	100.01	9.81068	63
6.	120.00	8.4	1420.00	100.00	9.81070	65

No.	Temp. gas F°.	H ₂ S grs. per 100 cu. ft. crude.	H ₂ S & SO ₂ in grs. per 100 cu. ft. purified.	Stain with lead acetate.
1.	75	150	3 None	None
2.	78	120	2 None	None
3.	76	105	2 None	None
4.	76	90	2 None	None
5.	75	80	2 None	None
6.	75	150	3 None	None

an insufficient covering of the purifying surface. From this series of tests it appears that 8.4 liters per square foot give the best results. Lower amounts may prove effective in large installation, for in this case approximately 120.00 liters of the wash liquor per 24 hours was required to properly flush all the absorption surface. In case the latter object is attained we see no reason why a smaller amount of solution is not sufficient, containing, as it does, an excess of sulfur dioxide.

Table C shows a gas rate varying from 20.64 to 1014.70 cu. ft. in 24 hours for each square foot of exposure area. From the data, approximately 1,000 cu. ft. of gas can be handled per square foot per 24 hours. The hydrogen sulfide will run from 3 to 5 grains per 100 cu. ft., but such low amounts cannot be objectionable.

no secondary washer is absolutely necessary since nearly all the sulfide is removed in the primary washing. Practice might show, however, that more efficient operation is secured by connecting two washers in series and passing the gas through much more rapidly. No. 6 of Table F was devised to show a running formula for a tubular washer, showing approximately the amount of solution, rate of gas flow and dioxide saturation found by experiment to give good results.

Now the great point about this washing system is that on ordinary washers where absolute contact is obtained about 1,000 cu. ft. of gas can be washed per square foot per 24 hours. This is something that should attract the attention of every gas man. A plant with a 10 million daily capacity would require roughly 10,000 ft. of absorption area, and by the use of some

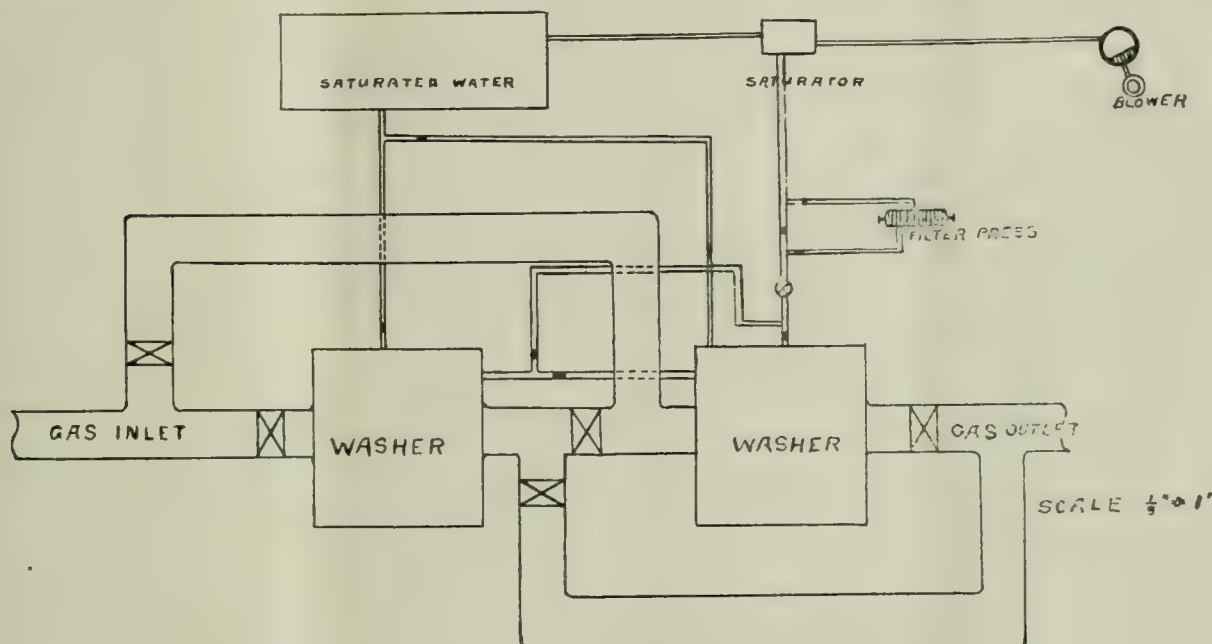


Fig. 1—Layout of Liquid Purification Plant.

Table D is an illustration of varying liquor, and Table E of varying gas temperatures. In D, the variation was from 35° F. to 83° F., and in E. 55° F. to 88° F. Both of these tables bear on one factor: The temperature of reaction. It is generally realized that most reactions are hastened by the application of heat, but in this work the difference was so slight that it could not be detected. We might then venture to assert that this reaction of hydrogen sulfide and sulfur dioxide can take place when the temperature of the gas or the solution ranges between 33° F. and 100° F. The upper limit may be even higher, but purifying temperatures above 100° F. are an uncommon occurrence in water gas practice and as for the lower limit it is absolutely fixed.

Table F shows a heavy variation in the hydrogen sulfide content from 80 to 150 grains per 100 cu. ft. of the crude gas. It may be that an excess of solution was used, but the tests showed practically no difference in the purified gas. This tends to show that

of the washers on the market at present, the above area would be lessened considerably.

Effects on the Quality of the Gas.—Another point of great importance is the effect of a sulfurous washing on the quality of the gas.

It was found that the carbon dioxide in the washed gas was .05 per cent lower than in the crude. This difference is probably due to the presence of the acid hydrogen sulfide in the crude gas. As this is removed with the carbon dioxide the results for carbon dioxide in crude gas are high. Therefore the washing has practically no effect on the carbon dioxide content. The decrease of illuminants is .09 per cent, due to washing. Since this decrease is less than a tenth of 1 per cent, it need not be considered a serious objection. It is apparent then that sulfurous acid has very little effect upon the hydrocarbons.

The Required Plant.—Two types of washers considered by the writer seem to be well adapted to supply the one essential requirement of this process—perfect

contact between the liquor and the gas. The first washer is manufactured by the Bartlett Hayward Company and is known as the Feld centrifugal. It was designed and used primarily in the Feld process outlined at the beginning of this paper. The other prominent type is one handled by the Western Gas Construction Co. and is known as a bubble washer. The liquor in this type is stationary, simply overflowing at any desired rate, while the gas enters a gland or series of glands in the apparatus from which it is forced upward through three concentric perforated plates. This bubbling action breaks the gas up to a fine foam and splendid contact is assured. These washers are very compact and are built in sizes large enough for all practical purposes, ranging from a few thousand to 10 million daily capacity. The maximum height of the largest sizes is 5 ft., so no pump is required to introduce the wash liquor, for by placing the storage tanks at a very slight elevation the liquor will enter by gravity. The glands can be removed very easily so that the cleaning is comparatively simple.

From this accompanying diagram (Fig. 1), the layout of the plant can be readily seen. A small sulfur burner with a small fan attachment is located at some little distance from the main installation, in order to eliminate all danger of fire. This burner will have a capacity of approximately 100 lbs. of sulfur per hour or a grate area of approximately 20 sq. ft.

The sulfur dioxide line leads to a small tower or bubble washer and is thoroughly mixed with the exhausted liquor, which then passes into the storage tanks. If a bubble washer is used to purify the gas, the stock tanks will have an elevation of a few feet, so that the liquor will flow by gravity into the washer. If the Feld washer is used, however, a pump must be installed to supply the wash liquor.

The Feld washer requires from 6 to 10 H. P. as an operating force for the centrifuge arrangement, and this forms one objection when it is compared with the bubble washer, although the latter has a certain amount of back pressure which is an absent quantity in the Feld apparatus. The washers in duplicate are connected so that they can be used together or separately. This means by-passing both the liquor and gas lines. The gas then passes on to the meters and the liquor is pulled through a small pump and forced through a filter press or it by-passes the press to the bubble washer to be saturated again with sulfur dioxide. Thus the same liquor can be used repeatedly and fresh water need only be saturated occasionally. The sulfur may be removed constantly, or it can be carried in the liquor up to a certain concentration and then filtered. The former course seems advisable, for if the sulfur was carried in the liquor for any time it would settle out in the saturating water and in the storage tanks.

The space occupied by this plant is somewhat less than 1,000 sq. ft. of ground area, and 15 ft. elevation for the bubble washer type, or an elevation of 30 ft.

for a small portion of that ground space, if the Feld washer is used.

The temperature regulations which are considered so important for the present purification need not be so rigidly observed in the proposed plant. The only requirement in this line is a temperature above freezing. Approximately one ton of sulfur is recovered from a 10 million capacity plant per 24 hours. This sulfur can be dried and packed on the purifying floor and stored in any dry place to await shipment.

The labor required is the service of two intelligent men for at least 18 hours of the 24. By this we do not mean constant attendance, but constant supervision.

Now the advantages of this system are as follows:

1. The same gas saturated liquor can be used repeatedly.
2. The plant as regards space and apparatus is very small.
3. Very simple reactions, instantaneous and independent of temperature.
4. Removes the necessity for handling large masses of solids.
5. Produces all the sulfur as a by-product, and this pays the cost of operation.
6. Makes clean gas.
7. Reagent simple and inexpensive.
8. Easily operated and requires no expensive skilled labor.
9. If the Feld washer is used, there is practically no back pressure in the system.
10. Its use means small investment and consequently low interest and depreciation.

These advantages we think will appeal to every gas man and will open for him a new field of endeavor.

The London Statist gives the following figures on the Lancashire cotton trade activity: The first half of this year has been a busy and profitable period for cloth manufacturers, the shipments being 3,276,359,000 yards, against 3,316,094,700 yards in the same six months of last year, and 2,864,158,400 yards in 1910. It may be said the export trade in 1911 established a record. Large buying has transpired this week in Manchester for India, especially in fine fabrics, shippers being willing to pay higher prices and give longer delivery. Spinners of yarns have been hampered by the raw-cotton situation, and although a fair amount of business has been done, the margin of profit has tended to be narrowed. The demand for abroad at the moment is very encouraging, the exports for the past six months being 124,605,800 lbs. against 112,627,800 lbs. last year, and 93,415,100 lbs. in 1910. About 100 spinning companies took stock at the end of June, but many concerns do not issue balance sheets. According to a table of 30 mills the profit on share capital works out at 14.78 per cent per annum, and on share and loan capital combined the profit is 10.88 per cent per annum, after allowing interest on loans.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

IV.

THE DETERMINATION OF ZINC IN ORES.

In both the volumetric and gravametric methods for the determination of zinc ores, the difficulty lies in the separation of the zinc from those metals which commonly accompany it in nature rather than the actual determination of the metal.

In the volumetric method, wherein the zinc, as a chloride in the presence of hydrochloric acid, and ammonium chloride, is titrated with potassium ferrocyanide, all those metals which form insoluble ferrocyanides—practically all the metals, indeed—must be absent. Similarly, in the precipitation of ZnNH_4PO_4 in the absence of free ammonia for the gravametric determination of the metal, all those metals which form insoluble phosphates must be absent, *i. e.*, all but the metals of the alkalis.

This separation of the zinc is best accomplished by the removal of silica and gangue, and then of the metals of the hydrogen sulphide group by precipitation, followed by the precipitation of zinc—as sulphide in the presence of acetic or formic acids thereby separating it completely from the members of its own and subsequent analytical groups. After the separation of zinc as sulphide, its determination either by titration or gravimetrically is simple.

The Volumetric Determination of Zinc.—The method found to be most satisfactory by the writer is that of Waring, with very slight modification. It is applicable to ores of all kinds, whether they be the usual fairly pure sphalerites (blendes) or the most complex sulphides or refractory Franklinites.

The titration is based upon the following reaction:
 $2\text{ZnCl}_2 + \text{K}_4\text{Fe}(\text{CN})_6 > \text{Zn}_2\text{Fe}(\text{CN})_6 \times 4\text{KCl}$,
 the ferrocyanide of zinc being thrown down, best from hot solution, as a pure white precipitate. The first excess of $\text{K}_4\text{Fe}(\text{CN})_6$ is detected through the appearance of a brown coloration in a drop of uranyl acetate upon a "spot plate" when a drop of the titrated solution is added. The brown coloration is due to the formation of the very strongly colored uranyl ferrocyanide. The uranium salt must be used as an outside indicator, because its compound with the $\text{Fe}(\text{CN})_6$ radical is insoluble.

Preparation and Standardization of Solutions.—1st. Potassium ferrocyanide, 21 gms., of the "c. p." crystallized salt are dissolved and made up to a litre and the solution thoroughly shaken, and, if cloudy, allowed to settle.

2d. Indicator. Four (4) gms. of uranyl acetate are dissolved in 100 cc. of water.

Standardization.—The so-called "c. p." zinc is ordinarily entirely too impure for use as a standardizing material. A standard zinc ore, to be run exactly as the analysis itself is run is best. Failing that the best grades of pure zinc oxide give very satisfactory results, and its use will be described.

Since zinc oxide is slightly hygroscopic, a few grams of it should be ignited in a platinum crucible for several minutes, cooled in a dessicator and placed in a glass stoppered sample tube.

Samples of 0.25 gm. (of which 0.8035 is zinc) are weighed into 400 cc. beakers and dissolved in 10 cc. concentrated HCl and water. When solution is complete, the whole is diluted to 200 cc., a piece of litmus paper added, and neutralized with ammonia, after which an excess of 3 cc. of concentrated HCl is added and the solution heated to just below boiling and titrated. If the titration is unduly prolonged, the solution should be reheated.

The ferrocyanide solution should be of such strength that 1 cc equals about 0.005 gm. of zinc, and since

$$0.25 \times 0.8035 = 0.2008$$
 then $\frac{0.2008}{0.005} = \text{about } 40 \text{ cc. of}$

solution will be required.

Even though the approximate volume of ferrocyanide required is known, it is well to reserve a portion of the solution and add a little at the time the end point is passed, the last of the reserve being added when the final end point is near, and the titration finished drop by drop. It is advisable to do this so that the titrations of standard and sample may be made under as nearly identical conditions as possible, thereby avoiding the errors which are apt to arise through variations in the composition of the ferrocyanide of zinc.

If, at the end of the titration and after standing a short time, the brown color appears in drops previous to the last one, 0.05 cc. (one drop) should be deducted from the final burette reading for each drop in which the color shows.

Since an appreciable excess of $\text{K}_4\text{Fe}(\text{CN})_6$ is required to turn the indicator, a "blank" titration should be run, using all reagents in equal quantities, but omitting the zinc. The writer subtracts 0.35 cc. from all burette readings, taking care to have solutions of

$$\text{weight ZnO} \times 0.8035$$
 about the same bulk in all cases. $\frac{\text{cc. K}_4\text{Fe}(\text{CN})_6 \text{ used}}{0.005} = \text{zinc standard (about 0.005 gms.)}$

Treatment of the Ore—When the Ore is Completely Decomposable by Acids.—Samples of 0.5 gm. ore are placed in 250 cc. Erlenmeyer flasks and boiled on the hot plate with 10 cc. HCl and a few drops of HNO₃ until the residue is white, when 5 cc. concentrated H₂SO₄ are added and the whole evaporated to copious fumes of sulphuric acid. HCl and HNO₃ must be completely eliminated at this point.

After cooling, 50 cc. of water are added, the flask rotated until everything soluble has dissolved, and the silica (and PbSO₄ if present) filtered off and washed. To the solution is added two 1-inch squares of clean aluminum foil with the corners turned up, and the solution boiled until it is colorless and all the metals of the copper group are precipitated. A piece of aluminum is then placed in a filter and the hot solution poured through, the precipitate being washed with boiling water. In this way arsenic, antimony, bismuth, copper, cadmium and traces of lead are removed, and the iron is reduced from the ferric to the ferrous condition.

The solution, which should not exceed 100 to 150 cc. is caught in an Erlenmeyer flask. A drop of methyl orange is added, and then, slowly a 10 per cent solution of NaOH until just alkaline, when it is just acidified with 20 per cent formic acid, and an excess of 2 cc. of the formic acid added. The whole is then heated to 70-80° C. and H₂S gas passed in under pressure. (This is accomplished by fitting a delivery tube reaching to the bottom of the flask, with a one-holed rubber stopper, allowing the gas to bubble through the solution for a moment and then pushing in the stopper and allowing the whole to stand for from 10-15 minutes).

The ZnS should appear as a white granular precipitate, settling rapidly and cleanly, and filtering readily. It is filtered off and washed rapidly with hot water. The filter paper is then opened out and spread upon the inner wall of a large beaker. As much of the precipitate as possible is washed into the bottom of the beaker by a stream from the wash bottle, and then 10 cc. concentrated HCl is poured slowly over the paper, and washed out with hot water.

When all the ZnS is dissolved, and the paper washed clean, the latter is removed, the solution is boiled to expel H₂S, neutralized with ammonia, acidified with a 3 cc. excess of HCl, made up to 200-250 cc. and titrated exactly as in standardizing.

$$\frac{\text{Vol. of sol. used} \times \text{standard}}{\text{weight of sample}} \times 100 = \% \text{ Zn.}$$

It is always desirable to hold a part of the solution in reserve, going beyond the end point with the main portion, and adding the reserve portion and the ferrocyanide solution from the burette alternately until finally, when all of the reserve has been added, the reaction is very close to its end and may be finished drop by drop.

Gravimetric Method for Zinc.—This is most desirable when a low percentage of zinc is present, as in the case of ores of metals other than zinc, metallurgical products carrying zinc, etc., but gives splendid results for all zinc ores as well.

The decomposition of the ore, the removal of silica, the precipitation of the heavy metals by aluminum, and the precipitation of zinc as ZnS is carried out exactly as in the volumetric method described above. The ZnS precipitate is then thoroughly washed, dissolved as before, and the solution boiled to expell H₂S, filtered through a small paper to remove any filter fibers and particles of precipitated sulphur. To the resulting solution (less than 100 cc.) two drops of litmus solution are added, and the whole made just alkaline with ammonia, and then just acid with nitric acid. An excess of (NH₄)₂HPO₄ (or NaNH₄HPO₄, microcosmic salt) is then added, when the solution will become alkaline, and a precipitate appear. Upon warming, the flocculent precipitate of phosphate of zinc changes readily and completely into the beautifully crystallized ZnNH₄PO₄. After standing until the solution is cold, this precipitate is thrown upon a weighed Gooch crucible. The precipitate may be dried to constant weight at 100° to 105° C. and weighed as such, but the writer prefers to ignite it to Zn₂P₂O₇ by placing the Gooch and precipitate inside a large porcelain or iron crucible and heating the outer crucible with the full flame of a bunsen burner. This gives about 300° C.

$$\frac{\text{Wt. ZnNH}_4\text{PO}_4 \times 0.3664}{\text{Wt. sample.}} \times 100 = \% \text{ Zn}$$

$$\frac{\text{Wt. Zn}_2\text{P}_2\text{O}_7 \times 0.4291}{\text{Wt. sample.}} \times 100 = \% \text{ Zn}$$

The precipitate of ZnNH₄PO₄ is readily soluble in fine ammonia (quite the reverse of MgNH₄PO₄, which is less soluble in ammonia than in water). This explains the necessity of adding the ammonium phosphate (itself an alkaline salt) to the slightly acid zinc solution. In the case of low percentages of zinc Waring recommends that the precipitate of ZnS be placed, with its filter paper, in a weighed porcelain crucible at the front of a muffle, where the paper is burned and the sulphide roasted to ZnO without loss of zinc or formation of basic sulphate. After the complete disappearance of the filter paper, the crucible is moved back in the muffle and then removed, cooled and weighed. For those unusual ores of zinc which do not yield all their zinc and acids, fusion must be resorted to in order to get complete decomposition. Half gram samples are treated with nitric and hydrochloric acids as usual, and evaporated dry, taken up with HCl and the residue filtered off and washed. The paper is burned and the residue fused with about a gram of Na₂CO₃ in a platinum crucible. The result is taken up with water and sulphuric acid added, the solution added to the original filtrate and the whole

evaporated to heavy fumes of sulphuric acid. From this point the analysis is as usual.

The fusion with Na_2CO_3 decomposes any zinc silicate or spinel, the zinc going to the soluble zincate, Na_2ZnO_2 .

THE ACCURATE VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID IN PHOSPHATE ROCK.*

By JOHN G. FAIRCHILD.

The method of determining the phosphoric acid content of phosphate rock here described is a modification of Pemberton's caustic alkali titration, which has the great advantage of being quicker than other volumetric or gravimetric methods. The difficulty experienced in the use of the Pemberton method has been invariably a low result compared with that obtained by the standard method of weighing the phosphoric acid as magnesium pyrophosphate. After close observation of the successive operations whereby the yellow precipitate is dissolved in an excess of standard alkali and this excess titrated after addition of a few drops of phenolphthalein, it was noticed that the final end point was considerably delayed, and this was the more marked the greater the amount of phosphoric acid present or the larger the aliquot parts taken.

In the belief that if this behavior of the indicator toward phosphoric acid could be overcome the method would be very accurate, the suggestion of Sutton¹ was adopted, namely, to precipitate out the phosphoric acid with barium chloride in excess before titrating the excess of alkali. The results stated below show how the method is improved by this modification.

In the first place, low results being obtained in dealing with phosphate rocks by standardizing the alkali solution against microcosmic salt in the old way, it was thought possible that the other salts in the rock solution interfered with the titration. A rock solution whose phosphoric acid content was accurately determined gravimetrically was taken as the standard. The average of four results (32.69, 32.82, 32.88 and 32.93) obtained by using different aliquot² parts of a 2-gram solution was found to be 32.83 per cent. P_2O_5 . Double precipitations were made after weighing the first precipitate, any calcium sulfate or silica being removed by its solution in sulfuric acid with alcohol. The second weights were only 0.1 to 0.3 mg. less, so that this correction could be disregarded.

The next step was to take an aliquot part, preferably 0.1 gram, add 20 cc. of strong ammonia (sp. gr. 0.90), make acid with 1:1 nitric acid and add slowly 25 cc. of warm molybdate solution (about 40° C.). The temperature of formation of the yellow precipitate here is most important, the limits being 45° to 55° C. After shaking for five minutes the precipitate is let stand till cool, then filtered through a 9 cm. No.

590 S. & S. paper and washed, once with a 2 per cent nitric acid solution and then with a 2 per cent potassium nitrate solution till the washings cease to redden blue litmus. Paper and precipitate are then transferred to the original flask and dissolved in an excess of standard alkali; diluted slightly with cold water; three drops of phenolphthalein solution are added and one drop of methyl orange (to give a sharper end point). Excess of alkali is then titrated with standard acid, either nitric or hydrochloric. Next, about 8 cc. excess of alkali are again added and 10 cc. of a 10 per cent solution of neutral BaCl_2 , which is usually sufficient to precipitate all the phosphate, the molybdate and also any carbonate. The important feature is the elimination of the phosphate. After again titrating the excess of alkali the two readings show 32.6 cc. and 33.1 cc. The results of several determinations gave this difference of 0.5 cc. Dividing the amount of P_2O_5 present, 0.03283 gram, by 32.6 and by 33.1 gives two values per cubic centimeter, namely 0.001007 and 0.000992 gram P_2O_5 , a difference of 1.5 per cent.

Again, taking the value per cubic centimeter as 0.001007 gram P_2O_5 and multiplying this by 33.1, the correct number of cubic centimeters required for 0.1 gram of the standard rock solution, the percentage of P_2O_5 found is 33.33, which is 0.51 per cent too high in P_2O_5 , or a 1.5 per cent actual error corrected by the use of BaCl_2 .

A solution of microcosmic salt was then prepared by dissolving 2.088 grams in some water containing 40 cc. 1:1 nitric acid and diluting to 500 cc. Several portions of 235 cc., equivalent theoretically to 0.03546 gram P_2O_5 , were taken and their content, determined gravimetrically, was found to be 0.03575 gram P_2O_5 . Exactly the same value was found by using 50 cc. of solution. A volumetric determination was now made on 25 cc., which required 35.5 cc. of alkali, barium chloride not being used. Excess of alkali was again added with 10 cc. of BaCl_2 , and the excess titrated. The result of the second titration was 36.0 cc. Multiplying the value of the alkali solution previously obtained against the standard phosphate rock we have $36.0 \times 0.000992 = 0.03571$ gram P_2O_5 , which is the exact amount taken for analysis. If the first burette reading is used we have $35.5 \times 0.000992 = 0.03522$ gram P_2O_5 , a difference of 0.5 per cent of P_2O_5 , or 1.5 per cent actual error, as before.

Although this calculation proves that microcosmic salt can be safely used in standardizing the alkali solution, still, in order to show more strongly that such salts as calcium nitrate have no effect on the titration figure, sufficient pure dry calcium carbonate was added to the nitric acid solution of the microcosmic salt to form tricalcium phosphate with all the phosphoric acid. The same aliquot portions were taken, precipitated, and titrated with these results:

Without BaCl_2 , 35.5 cc.; after addition of BaCl_2 , 36.0 cc. These check the results first obtained.

The value of the alkali solution having in this way

*From the Journal of Industrial and Engineering Chemistry, Volumetric Analysis, 9th Ed., p. 113.

²Pipettes used were standardized to the flask.

been fixed very accurately, analyses of a series of eight phosphate rocks (from different localities in order that all probable variations might occur in the composition of the rock solution) were made in the regular way by both volumetric and gravimetric methods. Two grams of the rock powder were put with a little water in a small covered casserole and digested on the steam bath with 40 cc. of 1:1 nitric acid for 20 min-

TABLE I.

Volumetric, per cent.	Gravimetric, per cent.	Differences.
31.68	31.70	-0.02
25.42	25.74	-0.32
31.79	31.99	-0.20
14.40	14.34	+0.06
24.83	24.67	+0.16
20.66	20.42	+0.24
24.43	24.49	-0.06
37.82	37.93	-0.11
		Sum, -0.25

Average difference = 0.03 per cent.

utes or more. The filtered solution was made up to 200 cc., a portion amounting exactly to 0.1 gram being taken for the volumetric and 0.5 gram for the gravimetric determination. In Table I will be found the results of single determinations.

Examination was next made of the insoluble residues. Four of these were combined and the papers were ashed in a large platinum crucible and fused with sodium carbonate. Silica was removed by evaporation of the acidified solution in a porcelain dish, the residue taken up with hot 1:1 nitric acid and test made for P_2O_5 . Only a trace was found. The papers of the second four were ashed, the silica volatilized with HF and H_2SO_4 , the HF being practically all expelled by repeated evaporation on the steam bath. After oxidation with HNO_3 , filtration, addition of ammonia and about 10 grams of NH_4NO_3 , the P_2O_5 found after dividing by 8 was 0.05 per cent. Several other tests have been made of residues insoluble in hot nitric acid and only once was as much as 0.10 per cent found, the usual result being no more than a trace.

The curve below shows the effect of $BaCl_2$ on the titration when increasing amounts of phosphate solution are used.

These are the actual percentages:

Portions (gram)	0.04	0.100	0.150	0.200	0.250
With $BaCl_2$	33.02 ¹	32.84	32.84	32.84	32.84
Without $BaCl_2$	32.50	32.34	32.14	32.14	32.01

The following results compare the two methods just described, the old method of weighing the yellow precipitate direct and Blair's method² of reducing the molybdic acid followed by titration with $KMnO_4$. The factor used for P_2O_5 in the ammonium phosphomolybdate was 0.3782. The yellow precipitate was washed well with 2 per cent nitric acid and dried in a porcelain Gooch crucible at 125° C. to constant weight.

Weight as ammonium phosphomolybdate.		
	Gram.	Per cent. P_2O_5
Portion taken	0.250	32.66
Fresh sample	0.500	32.70

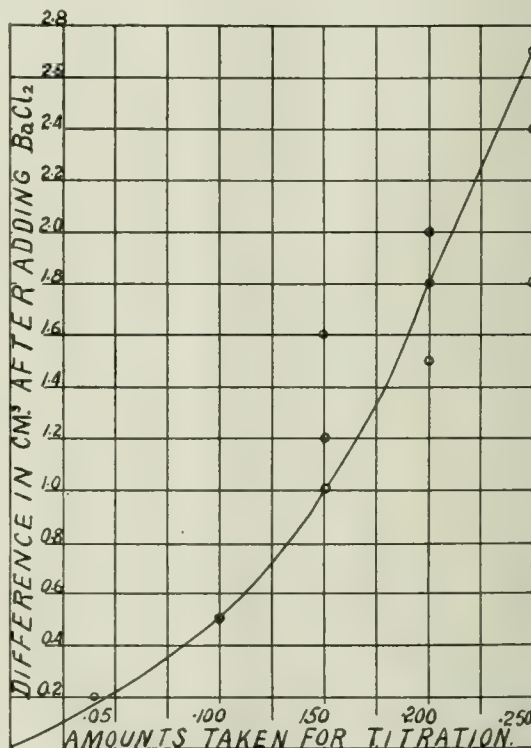
¹Single determination. About 0.2 per cent high. See curve.

²Analysis of Iron, 6th Ed., p. 92.

REDUCTION METHOD.	
Gram.	Per cent. P_2O_5 .
0.025	32.94
0.050	32.94
0.050	32.51
0.050	32.51

Blair's reduction method¹ gives accurate results when extreme care is taken to wash the yellow precipitate entirely free from the molybdate precipitant. Inasmuch as the portion taken here is very small, any slight difference in cubic centimeters of $KMnO_4$ used is multiplied by a large factor four times the factor for the caustic alkali titration. A difference of 0.35 cc. on a 0.05 gram portion gives a difference of 0.40 per cent in P_2O_5 content.

It is important to bear in mind that the barium phosphate precipitate hydrolyzes rather rapidly, so that the titration should be finished in 15 minutes. If



Curve Showing Effect of $BaCl_2$.

let stand an hour or more the pink color returns to the indicator. The reaction is probably like this: $Ba_2(HPO_4)_2 \times 2HOH = Ba(OH)_2 + Ba(H_2PO_4)_2$. The phenolphthalein is then affected by the barium hydrate. With precipitates containing more than 0.035 gram P_2O_5 it requires more care in order to strike the true end point. The plan followed above was to close the flask and shake it violently a few minutes, keeping it cold. With smaller precipitates there is no difficulty.

The least amount of molybdate solution necessary to completely precipitate 0.030 gram of P_2O_5 was found to be 20 cc. One cc. of this solution contains 0.048 gram HO_3 and will precipitate, theoretically, 0.002 gram of P_2O_5 . When only 15 cc. were used on a 0.1 gram portion of the standard rock solution 25.5 cc. of alkali were required for solution of the phosphomolybdate. On adding 5 cc. more of molybdate

¹Factor MoO_3 ; Fe, 0.85714.

solution to the filtrate and titrating the precipitate, 7.2 cc. more of alkali were used, a total of 32.7 cc., whereas the correct figure was 33.1 cc. To insure a noticeable excess 25 cc. of the molybdate solution are added.

By allowing 20 minutes for solution of the rock the time for a single determination will average not more than one hour.

As a final test, the amount of error due to expansion of the standard solutions was fixed. A standard alkali solution was transferred to a 100 cc. flask up to the mark and its temperature taken. The solution was then heated exactly 10° and the rise in volume noted on the neck of the flask. This increment was then withdrawn by a pipette and its value found by running in from a burette enough to reach the top mark again. This difference due to 10° C. was found to be 0.2 cc., an error altogether negligible.

In conclusion, it is seen that the greatest accuracy possible by the gravimetric method is 0.50 per cent, or 0.15 per cent of the P_2O_5 content, and it varies to 0.75 per cent, or 0.25 per cent P_2O_5 . The accuracy of the caustic alkali method is a trifle over 1 per cent actual error, or a difference of 0.30 per cent P_2O_5 in the rock.

STANDARD SOLUTIONS.

Caustic Alkali.—Thirty-one grams of the C. P. soda sticks dissolved in water and diluted to 2 liters: 1 cc. equals about 0.001 gram P_2O_5 . The small amount of CO_2 present, about 0.12 per cent, is negligible.

Nitric Acid.—Practically a 2 per cent solution which is diluted till 1 cc. equals 1 cc. alkali solution.

Phenolphthalein.—A 1 per cent alcoholic solution.

Methyl Orange.—A 0.1 per cent solution.

Molybdate Solution.—One hundred grams MoO_3 , 144 cc. NH_4OH (sp. gr. 0.90), and 271 cc. H_2O ; 489 cc. HNO_3 (sp. gr. 1.41) and 1.148 cc. H_2O .

According to the Belfast (England) Evening Telegraph four large boilers at Harland & Wolff's Ship-building Works on Queens Island have been adapted for oil fuel in order to be independent of coal as a fuel. Using coal for fuel, one of these boilers evaporates 16,000 lbs. of water an hour and the other three 12,000 lbs. each, and with liquid fuel they will generate 4,000 horsepower per hour. The work of installation is so simple that it can be carried on without letting the steam out of the boilers. The steam-jet system is used, which it is claimed will recover 68 to 74 per cent of the calorific value of the fuel used. The oil enters the boiler through a branch pipe and is given a whirling motion by the prolonged spiral stem of the valve spindle, the amount of oil being governed by a handwheel at the end of the spindle. The steam enters at another valve and passes through slots in the cylindrical part of the cone. All the oil passing through the burner is thus steam jacketed. One or two men can attend to a dozen boilers burning liquid fuel

DETERMINATION OF CELLULOSE.*

According to an abstract in the *Journal of the Society of Chemical Industry* (Vol. xxxi, 9), J. König and F. Hähn have carried out a comparative series of determinations of the cellulose in a number of typical raw materials by the principal methods which have been proposed and adopted by various authors.

The raw materials were first extracted with cold and hot water, then with benzine and alcohol; they were dried and allowed to absorb moisture from the air. The materials tested comprised beech, oak and fir woods, the barks of these woods, sulphite wood-pulp, cotton, flax, hemp and jute. The methods employed were those of Weedne-Henneberg ("crude fibre"), Tollens-Dmochowski, König, also the direct treatment with ammoniacal hydrogen peroxide, and the methods of Cross and Bevan (chlorination), Schulze (potassium chlorate and nitric acid) and Müller (bromine water and ammonia). Of these methods the Weende-Henneberg and the method of direct treatment with ammoniacal hydrogen peroxide yield products which can hardly be described as cellulose at all, being still rich in lignin, while certain of the others yield celluloses more or less profoundly modified by oxidation and still containing appreciable residues of the non-cellulose constituents of the raw materials.

The authors have made a very full investigation of the nature of the cellulose products obtained, not only by qualitative tests, which are of little value, but also by quantitative determinations of elementary composition, calorific value, methyl value, and pentosan-content (furfural value). Comparison of these results with those found for the raw materials afforded a measure of the extent to which the various noncellulose groups had been removed.

Consideration of this side of the problem raises the question of a definition of "cellulose." According to the authors' views, the original materials contain: "true cellulose," lignin, hemihexosans and pentosans, together with cutin in the case of bark tissues. They content that only by a regulated hydrolysis followed by oxidation can the true cellulose be freed from the other constituents.

Although the methods depending on oxidation without "hydrolysis" (e. g. Cross and Bevan's chlorination method) may under favorable conditions eliminate the greater part of the lignin, such methods fail to remove most of the hemihexosans and pentosans, and the higher yields thus obtained depend on the presence of these impurities; moreover, the cellulose obtained possesses the properties of a pronounced oxycellulose. For instance, Cross and Bevan's method yielded 100 per cent of cellulose from cotton, whilst König's method yielded only 88.27 per cent, in the form of a friable powder. Hence it is contended that cotton is not substantially composed of true cellulose

*From Paper.

but contains very considerable proportions of hemi-hexosans.

In addition to the quantitative tests mentioned above the authors also propose the following new method for testing the purity of the cellulose preparations. The cellulose is dissolved in a solution of zinc chloride in concentrated hydrochloric acid and the liquid is examined polarimetrically at intervals over a considerable period, the specific rotatory power being calculated. This, starting from about zero, gradually rises as hydrolysis proceeds, reaching a maximum after two or three days, then falling slowly, owing to condensation, until the liquid becomes opaque.

Those preparations which reach the highest maximum specific rotation represent the purest forms of true cellulose, since pentosans and other impurities tend to lower the results. The cotton cellulose prepared by König's method showed a maximum $[\alpha]_D = 82.5^\circ$ after 72 hours, whilst cotton purified by Cross and Bevan's method showed a maximum of only 56.7° after 55 hours. Hydrocellulose and oxycellulose reach only low maximum rotations and the rotatory power changes rapidly. This supports the authors' contention that digestion with glycerin containing 2 Gm. of sulphuric acid per 100 Cc. at a temperature of 137° C., while eliminating the hexosans and pentosans, has practically no effect on the true cellulose, and that König's method, in spite of the low yields of cellulose obtained is the best one for the quantitative determination of that constituent.

Next to König's, the method of Tollens-Dmochowski is preferred, according to which hydrolysis by the Weende process if followed by oxidation with nitric acid; the hydrolysis of the hexosans and pentosans however is not quite complete.

The following incidental observations may be noted:—(1) Fir wood was the only fibrous material which was found to contain any notable quantity of methyl-pentosans, showing 4.48 per cent out of 13.72 per cent of total pentosans. (2) The following percentages of cutin were found in the bark tissues by dissolving the cellulose in acid zinc chloride; beech bark, 4.42; oak bark, 7.33; fir bark, 3.33.

The Eleventh Financial and Economic Annual, issued by the Japanese Department of Finance, shows that on December 31, 1909, there were 681 machine shops, 595 tool works, and 1,000 foundries and metal-ware establishments in operation throughout the Empire. These employed 13,688, 11,903, and 16,987 operatives, respectively, the women workers numbering 156 in the machine shops, 962 in the tool factories, and 1,863 in the foundries. The average wages of machinists and tool makers are not given in the report, but founders received 27 cts. per day in 1906, 31 cts. in 1907, 33 cts. in 1908, and $33\frac{1}{2}$ cts. in 1909. There were also 44 plants listed as "metal refineries," employing 1,196 operatives.

A METHOD OF EXAMINING CHINA WOOD OIL.*

By PARKER C. McILHINEY.

The examination of china wood oil to determine its quality and to detect the presence of foreign oil presents several difficulties. The iodine figure is not far removed from that of several other oils, the saponification figure is identical with that of many others and although the specific gravity and the refractive index are higher than those of almost any other fatty oil, the difference in these respects from some other oils is not sufficiently great to furnish satisfactory data in all cases.

The most marked characteristic of china wood oil is its property of solidifying readily under the influence of heat or when acted upon by iodine. Heating the oil to a temperature of from 240 – 280° C. and noting the readiness with which the oil jellies and the consistency of the jelly produced have been extensively used as commercial tests for grading the oil. It is difficult, however, to conduct such a test under conditions which will give numerical values to the results, these being usually stated in terms of the apparent hardness or softness of the jelly, or else in terms of the number of minutes required to jelly at some given temperature. The latter method is open to several serious objections and it is difficult to reproduce in a second experiment the conditions of the first.

The behavior of the oil when iodine dissolved in a suitable solvent is added to it, furnishes a well known qualitative method of identifying china wood oil and particularly of distinguishing it from linseed oil, but since the test as usually carried out gives merely a jelly, no quantitative results are obtainable from them.

It was thought that if this test could be made quantitative so that a separation could be effected between the solidified and the liquid resulting from the action of iodine upon the oil, a valuable and quantitative method of testing the oil might be obtained, particularly as such a test would be directly related to the most important and characteristic property of the oil. A series of experiments conducted with this end in view showed that acetic acid of $99\frac{1}{2}$ per cent strength or thereabouts was a solvent in which both the iodine and the oil could be dissolved and out of which the solidified product separated readily so that it might be removed from the liquid portion; furthermore, that this liquid portion could be dissolved in a petroleum solvent boiling under 80° C. while the solid product from the china wood oil was practically insoluble in this solvent. Based upon these facts the following method of analysis was devised:

Weigh into an Erlenmeyer flask about 5 grams of the oil to be examined, add to it 10 cc. of $99\frac{1}{2}$ per cent acetic acid and after warming it so that there is a perfect mixture of oil and acid, add to it 50 cc. of a

*From the Journal of Industrial and Engineering Chemistry.

solution of iodine in 99½ per cent acetic acid containing 15 grams of iodine per liter. The acetic acid solution of iodine should be warmed so that when added to the oil solution to be tested it will not chill it. Upon adding the iodine solution there results an almost instantaneous separation of some solid product from the solution in large amount. The solution is allowed to rest for half an hour to insure complete reaction and then 50 cc. of petroleum solvent (b. p. below 80° C.) added and allowed to mix thoroughly with the contents of the flask. The liquid is then drained off from the flask into a separatory funnel and another portion of 50 cc. of petroleum solvent added to the solid residue which has been allowed to remain in the flask so as to wash out of it the residue of liquid products; after pouring off this solvent the solid residue is extracted a third time with 50 cc. of petroleum solvent, the solutions being united in the separatory funnel. Water is now added to the contents of the separatory funnel and this causes a separation of the liquid into two layers, one of petroleum solvent carrying the liquid portions of the reaction in solution and the other of water united with acetic acid. This latter is drawn off and the petroleum solvent repeatedly washed with water till it is free from acetic acid and then shaken out with a solution of potassium iodide to remove free iodine which may be present; after a final washing with water it is transferred to a flask, the solvent evaporated off and the residue weighed. The weight of this residue is a measure of the proportion of those constituents of the oil under examination which are not solidified by the action of iodine.

Broadly stated, the process gives results showing that only a small fraction of china wood oil remains liquid at the conclusion of this process while other oils remain entirely liquid and soluble in the petroleum solvent and if the process be applied to known mixtures of a given sample of china wood oil with soya bean oil the proportion of soya bean oil may be determined with reasonable accuracy. In order to make such a determination, however, upon oils of unknown origin, it is necessary that the per cent of liquid products which may conveniently be described as "per cent of soluble iodides" of true china wood oil and also the variation in this per cent given by different varieties and samples of true china wood oil should be known. In order to investigate this matter it is necessary to obtain a considerable number of authentic samples of such oils and these samples are to be obtained only in China and in the other countries where this oil is produced. The method is, however, submitted as one suitable for the investigation of the oil and particularly as a method for determining the grade of the oil in respect to its most characteristic property.

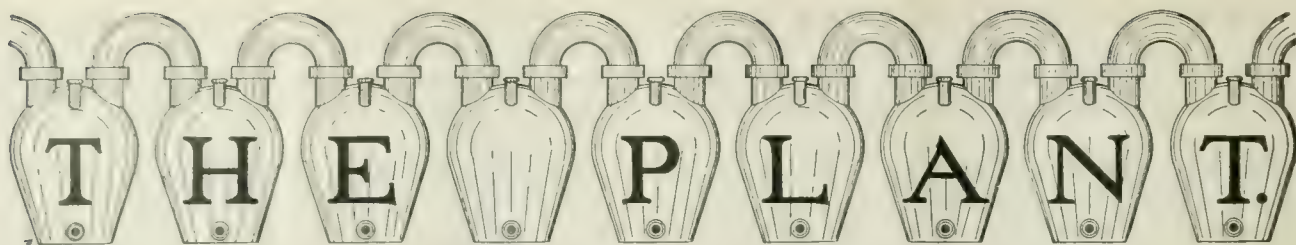
As the writer has been unable to obtain any considerable number of original small samples of the oil, he refrains from giving the exact figures obtained

upon the commercial samples which have been examined but hopes that others may apply the process to authentic samples as they are obtained.

CANADIAN FOOD ADULTERATION ACT.

Certain provisions concerning the adulteration of foods were added to the Canadian inland-revenue act in 1868 as an amendment and passed. As this was the foundation of all later acts a summary of the provisions may be interesting. Analysts were appointed in Halifax, Montreal, London (Ontario), St. Johns, Toronto and Quebec. The inland-revenue officers were to collect samples of goods suspected to be adulterated and submit them to the analysts. On receiving a certificate that these suspicions were well founded they were to seize and destroy the goods. The analysts were to report quarterly to the Minister of Inland Revenue at Ottawa, who was to present the results to Parliament annually. Dealers were obliged to give samples whenever requested, and the penalty for selling adulterated food was \$100 on the first conviction and \$200 for a subsequent offense. A manufacturer was to be fined \$100 for a first offense and upon a second conviction was liable to six months' imprisonment. The adulteration act of 1884 is in force today. It was amended in 1888, 1890, 1896 and 1900, but the changes were comparatively unimportant, being principally definitions. The new act provided for the appointment of a chief analyst, who was to be attached to the staff of the Inland Revenue Department at Ottawa. He was to be a final arbitrator whenever a question arose as to the correctness of any analyses made by a local analyst. He was to supervise generally the work of the laboratory of inland revenue and prepare from time to time bulletins setting forth the results of the collection of samples. These were to be issued to the public and contain the names of the venders from whom the inspectors obtained samples, as well as names of manufacturers when possible. The exact condition of each article examined was to be shown, together with the opinion of the analyst regarding the purity and fitness for the purpose for which it was sold. In all, 231 of these bulletins have been issued in 27 years.

A Brussels correspondent of the London Times reports that a financial group, including banks in Brussels, Antwerp, Liege, Paris and Lille has recently constituted in Brussels a company under the name "Union Allumettiere," with \$1,200,000 capital, to acquire control of the match manufacturing businesses in Belgium. At present the new company has acquired new match works with a general yearly output of about seven thousand million boxes, of which nearly one-third is for home consumption, the balance being exported chiefly to England, the Indies, and the East.



THE APPLICATION OF CHEMICAL CONTROL TO THE OPERATION OF WATER GAS PLANTS.*

This paper consists of data secured from the analyses of gases from carburetted water gas machines, extending over a period of four years, in the operation of three different gas plants, and the data obtained used as a means of arriving at a proper way to control the operation of water gas apparatus.

The analysis of the various gases from a water gas set gives positive information as to what the machine is doing, and a lead as to what is necessary to intelligently remedy any of the inefficiencies in its operation. It is not always possible to secure conditions for the economical operation of a water gas set, because of inefficient boiler system, blower plant, or other causes, but a systematic analysis of all conditions will yield good results.

It is possible during operation to secure 60 different samples of gas from one complete run and blow. Each sample has a certain value, and the first problem that confronts the engineer or chemist is to determine which of these 60 samples he needs to secure the information he is seeking, with the least possible work.

The second problem he encounters is how to tell, from the samples he has chosen, whether his analysis represents efficiency or inefficiency. It is safe to say that the majority of gas engineers and chemists use the gas analysis as a check on the quality of the gas, but do not attempt to apply it to locate the cause of trouble, if the quality suddenly drops. When the candlepower drops, the attempted solution is usually more oil, and at the time it is very probable that the machine is then overloaded with oil. There is for every temperature condition in a water gas set a certain definite amount of oil that the machine will take care of and convert into gas efficiently. Above this amount the proportion going into gas drops off rapidly producing a corresponding increase in cost of manufacture. This being true, it is a waste of time and money in trying to correct the inefficiency of the generator or superheater by deluging the carburetor with oil. What is true of too much oil is also true of too little. When not enough oil is being used to properly enrich the blue gas and utilize the heat in the carburetor and superheater, a large percentage of the oil is decomposed beyond the hydrocarbon point, forming lamp black and hydrogen.

One way of checking this condition is to calculate the percentage of blue gas in the finished gas, and such calculation will be taken up later.

From the results obtained during several years of operation on five machines the percentage of blue gas in the finished gas was between 72 per cent and 76 per cent. How very little it changes the make in juggling the oil so the percentage of oil gas varies 2 per cent. This being true, it must also be true that there is something far more important than a mere difference of a fraction of a gallon of oil from the normal, that changes and governs the make and quality of the gas.

Another problem is to determine what causes the various changes in the action of a water gas set. Some of these are well known and are often experienced; namely, stoppages due to formation and deposition of carbon and ash, formation of a film of insulating substances on the firebrick, spray trouble, which usually is easily remedied. An illustration of what could have been a serious form of spray trouble might be of interest.

On a carburetor which had been giving good results with the spray nozzle properly adjusted and kept clean, it became necessary to recheck. After rechecking black spots developed. On investigation it was discovered that the brick had been carried 2 tiers higher than before, and this caused the oil to be distributed unevenly. On removal of the two extra tiers of brick the conditions again became normal.

Inability to burn the coke in the generator is a condition often encountered and hard to deal with. One of the objects of this paper will be to apply the analyses of the various gases to show the cause for these conditions, and by the analytical data secure a definite series of formulæ that will answer the investigator in relative figures. A series of curves forming part of this paper furnish analytical data on the composition of every gas that can be secured from a water gas set, under several variable conditions. The samples were secured periodically at various points on the machine and the data plotted. There were 4 complete tests made. Each test covered a week's work, the samples being taken one day, the rest of the week being spent in watching results. Series of runs and blows were sampled every minute, at the top generator and top superheater, for one hour, which included the usual down run and generator charging. Three sets of samples were taken; one shortly after clinkering, $\frac{1}{2}$ way between periods of clinker and one shortly before the next clinker. The machine was allowed to make

*From the American Gas Light Journal.

directly into a small holder, and minute readings were made during the test run, to determine the make. The oil, coke, ash, etc., were carefully kept track of.

Temperature readings were made at the center of the generator, center of the carburetor and top of the superheater, each minute between clinkers and each $\frac{1}{4}$ minute during test run. From the data thus secured the plates were prepared.

The carbon at the bottom of the generator is, or should be, burned to CO_2 . The CO_2 passes up through the incandescent carbon, reacting with it, taking up carbon forming CO . This CO will be burned in the carburetor if the conditions are right. From these plates it is possible to calculate exactly what is happening in the machine.

In the first test 56.4 per cent of the fuel used in blasting was completely consumed in the generator; 29.1 per cent was used in heating the carburetor and superheater; while 14.5 was burned outside the machine.

These figures represent what is customarily called good operation. They were taken from an 11-ft. 6 Lowe type water gas machine, under the ordinary working conditions. The morning of the test the operator was asked his opinion as to the condition of the apparatus and passed it as "O. K."

Calculating from the analysis of the gas, we find that only 33 per cent of the generator fuel is used for gas making, while 67 per cent is used for blasting. Of this, 21.5 per cent goes out the stack as combustible gases. This denotes inefficiency. In actual weight that amounts to over 1 ton of coke. The coke on this day was 33.3 lbs. per 1,000. Taking out the loss, due to combustion occurring outside the machine, but not including the excessive amount of coke used in blasting, the coke per 1,000 would be 27.6 lbs.

It would be difficult for anyone not familiar with the chemistry of gas manufacture to pick, from the analyses submitted, those which are most necessary for proper control in the operation of water gas apparatus, and for everyday use the needed information must be secured with as few operations as possible. It will be found that a daily analysis of the finished gas is very useful in determining the quality of the gas sent out. When trouble occurs, attention should be given at once to the generator condition. Secure a sample of blue gas taken each minute during run. In the same manner secure samples of the blast gases from the generator and superheater. Examine these samples only for carbon dioxide, oxygen, carbon monoxide, in the blue gas for hydrogen, and the work can be accomplished in a short time. The amount of information that can be secured from these few carefully prepared analyses is astonishing. All but three sets of analyses have been eliminated; one blue gas and two blast gases.

It is evident that unless the exact way in which the fuel that has been used in the generator is known, we

cannot understand why, if the percentage of CO_2 is high or low. Take, for instance, Plate No. 25, with all the temperatures given it would be hard to locate the cause of the excessive amounts of CO_2 in the generator. In fact, unless there was a gas analysis at hand there would be nothing to indicate that the CO_2 was high, for, as Plate No. 1 shows, the temperatures are normal and do not indicate that there is any loss. The oil and coke being high show this loss, and the gas analysis gives a means of calculating the exact point at which the loss is taking place. Therefore, it is believed that the data thus secured must be reduced to a definite standard, which will represent the prevailing conditions.

Continuing the comparison, the oil used in the first test is high. The conclusion might be, without definite knowledge to the contrary, that the temperature of the carburetor was low, but raising the temperature on a guess may be the cause of having to recheck the machine in a short time because of the formation of excessive lampblack. It would be possible to enumerate numberless nearly right conditions, that to guess at the remedy would be dangerous to economical operation.

The following is a calculation of the distribution of fuel consumption in a carbureted water gas set, the purpose of which has been shown.

ANALYSIS OF BLAST GASES BY VOLUME.

	Generator.	Carburetor.	Superheater
CO_2	10.2	15.5	19.1
Oxygen	0.8	0.2	0.3
CO	15.0	6.3	0.5
Nitrogen by diff....	74.0	78.0	80.1

The percentage by weight is accomplished by multiplying each constituent by its specific gravity. The sum of these products gives the weight of the gas, and, when divided by 100, the specific gravity. By dividing the weight of each component part by the weight of the whole, the percentage by weight is secured. In the case of the generator gas we have:

CO_2 ... 10.2×1.529 sp. gr. = 15.55 + 112.23 = 13.7 Pct. by wght.
 O 0.8×1.105 sp. gr. = 0.88 + 112.23 = 0.8 Pct. by wght.
 CO ... 15.0×0.97 sp. gr. = 14.50 + 112.23 = 12.7 Pct. by wght.
 N 74.0×1.1 sp. gr. = 81.40 + 112.23 = 72.8 Pct. by wght.

112.23

ANALYSIS OF BLAST GASES, PERCENTAGE BY WEIGHT.

	Generator.	Carburetor.	Superheater.
CO_2	13.7	20.4	24.8
O	0.8	0.2	0.3
CO	12.7	5.2	0.4
N	72.8	74.2	74.5

ANALYSIS OF BLUE GAS.

	By volume.	Sp. gr. Wght.	Percentage by wght.
CO_2	$3.0 \times 1.529 =$	$4.6 \div 54.9 =$	8.5
O	$0.6 \times 1.105 =$	$0.7 \div 54.9 =$	1.3
CO	$41.7 \times 0.97 =$	$40.5 \div 54.9 =$	73.6
CH_4	$1.9 \times 0.57 =$	$1.1 \div 54.9 =$	2.0
H	$48.6 \times 0.0695 =$	$3.4 \div 54.9 =$	6.2
N	$4.2 \times 1.1 =$	$4.6 \div 54.9 =$	8.4

54.9

ANALYSIS OF FINISHED GAS.

	H_2	O.	CO.	CH_4	H.	N.
CO.	10.2	0.2	30.0	17.5	33.7	6.2

Since oil gas contains practically no CO from the gasifying of the oil, and at most never more than 1 to

2 per cent, the following calculation can be used with reasonable certainty:

Per cent CO in blue gas : Per cent in finished gas : : 100 :
X. Therefore, the finished gas is 72 per cent blue gas.

DISTRIBUTION OF COMBUSTION GENERATOR.

Percentage of carbon in CO₂ = 27.27

Percentage of carbon in CO = 42.80

Heat of combustion, carbon to CO₂ = 80,833 calories.

Heat of combustion, carbon to CO = 24,166 calories.

Using the analysis of generator blast gases; percentage by weight:

CO₂.. 13.7 per cent multiplied by percentage carbon in CO₂ (27.27 per cent) = ... 3.73 per cent

CO .. 12.7 per cent multiplied by percentage carbon in CO (42.80 per cent) = ... 5.43 per cent

9.16 per cent

The sum is the total carbon in these gases (9.16).

$3.73 \times 80,833 + 5.43 \times 24,166$

$9.16 \times 80,833$

erator.

The carbon in the CO₂ having been burned completely has given off all of its heat. Therefore it is multiplied by its total heat of combustion. The carbon in the CO has not been burned completely; therefore, it has not given off its total heat of combustion. It is multiplied by the heat of combustion of carbon to CO. If the sum of these two be divided by the product of the total carbon in the gas, and the heat of combustion of the carbon to CO₂, the result is the percentage of the total possible combustion that has taken place, at the point where the samples of gas were taken.

COMBUSTION IN GENERATOR AND CARBURETOR.

CO₂.... 20.4 per cent $\times$ 27.27 per cent = 5.56 per cent

CO..... 5.2 per cent $\times$ 42.80 per cent = 2.22 per cent

7.78 per cent

$5.56 \times 80,833 \div 2.22 \times 24,166$

$7.78 \times 80,833$

= 80 per cent

COMBUSTION IN GENERATOR, CARBURETOR AND SUPERHEATER.

CO₂.... 24.8 per cent $\times$ 27.27 per cent = 6.76 per cent

CO..... 0.4 per cent $\times$ 42.80 per cent = 0.17 per cent

6.93

$6.76 \times 80,833 \div 0.17 \times 24,166$

$6.93 \times 80,833$

= 98.7 per cent.

COMBUSTION OUTSIDE MACHINE.

100 per cent — 98.7 per cent = 1.3 per cent.

SUMMARY OF DISTRIBUTION OF COMBUSTION.

Per cent.

Blasting generator..... 59.2

Blasting carburetor..... 20.8

Blasting superheater..... 18.7

Outside machine..... 1.3

DISTRIBUTION OF FUEL—CALCULATING CARBON IN BLUE GAS.

CO₂. 8.4 per ct. $\times$ 27.27 per ct. = 2.29 per ct.

CO.. 73.5 per ct. $\times$ 42.80 per ct. = 31.46 per ct.

33.75 per ct. Total carbon in blue gas.

One cubic foot of air weighs .08069 lb. Multiplying this weight by the specific gravity of the blue gas, .55, gives the weight of 1 cu. ft. of blue gas, or, in this case, .044379 lb.; 1,000 cu. ft. weighing 44.379 lbs. This 44.37 lbs. of blue gas being 33.75 per cent carbon, contains 14.95 lbs. of that element. As the finished gas is 72 per cent blue gas, there is in every 1,000 cu. ft. of finished gas (14.98 $\times$ 72) or 10.8 lbs. of carbon taken from the generator fuel.

On the day of this test the coke ran 34.6 lbs. per 1,000. Deducting the 10.8 lbs. used for gas making, leaves 23.8 lbs. to represent that used in the blasting.

Dividing the 23.8 lbs. of coke used for blasting by the percentage distribution of combustion, gives the following summary for the complete distribution of fuel:

Per cent.

Fuel used for gas making 10.8 lbs..... 31.2

Fuel used blast generator 14.1 lbs..... 40.8

Fuel used blast carburetor 4.9 lbs..... 14.2

Fuel used blast superheater 4.5 lbs..... 13.0

Fuel burned outside machine .3 lbs..... .8

The above conditions would indicate that not enough of the coke is going into the gas, too much being used for blasting. The direct cause for this was a slight stoppage in the take-off pipe, allowing a free blast and retarding the exit of the gas. The first time that the distribution of fuel was calculated by the writer was on an occasion when temperature of the carburetor could not be kept high enough. The machine would not take care of the oil and gave considerable trouble. The following data was secured at that time:

Distribution of Combustion: Per cent.

Blasting generator .. 95.0

Blasting carburetor and superheater..... 3.8

Outside machine 1.2

Distribution of Fuel:

Gas making 31.8

Blasting generator 64.8

Blasting carburetor and superheater..... 2.6

Outside machine 8

This analysis showed what was needed to remedy this condition was to send a little more CO into the carburetor, and this required a little more or less blast. As the blast was 22 ins., it was reduced to 18 ins., and when the change had been made the following results were secured with a consequent drop in cost of manufacture:

Distribution of Combustion: Per cent.

Blasting generator 70.5

Blasting carburetor 15.9

Blasting superheater 4.55

Outside machine 9.00

Distribution of Fuel:

Gas making 36.4

Blasting generator 44.9

Blasting carburetor 10.1

Blasting superheater 2.9

Outside machine 5.7

On another occasion considerable trouble was encountered in keeping the temperature of the superheater down. On analysis it was found that an equal amount of combustion was taking place in both carburetor and superheater. Since the carburetor receives by far the greater cooling action from the oil, it was soon seen that too much blast was driving the gases through the carburetor without giving them time for the proper combustion and the trouble was corrected.

This particular test led to considerable experimenting on the subject of the formation of lampblack. It was the writer's privilege to direct the preparation of carbon filaments for the various types of incandescent lamps. One of the operations was to place the filament in a vessel, drawing a vacuum within $\frac{1}{8}$ -inch of the barometer. This vacuum was then relieved by allowing gasoline or hexane vapor to enter the vessel, until the pressure had gone up to 2 inches above a perfect vacuum. The filament was then heated by passing a current of electricity through it, until it was

incandescent. This decomposed the hydrocarbon vapor which formed in a thin, hard graphitic coating of carbon on the filament. This coating gives the filament its proper electrical resistance and increases its life.

On one occasion series tests were made to determine the effect of air on the decomposition of the hydrocarbon. It was found that with $\frac{1}{4}$ of an inch of air pressure a considerable quantity of lampblack was formed. With $\frac{1}{2}$ an inch large quantities of lampblack were formed, depositing on the sides and bottom of the vessel.

With the above in mind, it was noticed several times that, when the oil was started before the blue gas reached and filled the carburetor, considerable quantities of lampblack were seen in the overflow. This was with a comparatively low temperature in the carburetor and superheater. Somewhat the same principle is applied to the manufacture of lampblack commercially. The oil is burned in a reduced atmosphere. A gas maker can make more lampblack than is advisable and not know it, and the following calculation has been used advantageously to determine just how much excess lampblack is being formed.

The average percentage of CO in blue gas 45.4 per cent.

The average percentage of CO in finished gas, 32.9 per cent.

$32.9 : 45.4 : 72 : 100$.

The finished gas is 72 per cent blue gas.

The blue gas is 48.9 per cent hydrogen.

$48.9 \times 72 = 35.4$ per cent of hydrogen in finished gas, due to the blue gas.

Finished gas is 42.9 per cent hydrogen.

$42.9 - 35.4 = 7.5$ per cent of hydrogen in finished gas, due to decomposition of hydrocarbons into carbon and hydrogen.

Multiply this by 1,000 and secure the cubic feet per 1,000 of finished gas, which is 78.

Specific gravity of hydrogen is .0695.

One cubic foot of air weighs .0869 lbs.

$.0869 \times .0695 = .0056$, weight of 1 cu. ft. of hydrogen.

$.0056 \times 78 = .44$ lbs. of hydrogen per 1,000 cu. ft. of finished gas, due to the decomposition of the oil into carbon and hydrogen.

Assuming C_6H_6 as the average composition of the illuminants. The illuminants, being unsaturated hydrocarbons, are unstable and very easily decomposed. The following illustrates the nature of this decomposition:

(Methane) CH_4 , C_6H_6 , $C_{10}H_8$ (naphthalene)

(Carbon) C , C_6H_6 , H (hydrogen)

There are innumerable intermediate reactions, but always, if the decomposition be carried far enough, carbon and hydrogen will be formed.

From the above it is concluded that, for each part of hydrogen formed from the oil, there will be 1 part of carbon formed. In this case there were .44 parts of hydrogen formed. As carbon is 12 times as heavy as hydrogen, there would be $.44 \times 12 = 5.28$ lbs. of lampblack formed per 1,000 cu. ft. of finished gas.

As both the hydrogen and the lampblack thus formed were derived from the oil, there were $5.28 + .44 = 5.72$ lbs. of oil used to form 78 cu. ft. of hydrogen. The oil in this test ran 4.0 gals. per 1,000. By the application of the above calculation and the use of a few gas analyses, it was cut to 3.4 gals. per 1,000. The data secured for this paper are far too extensive to permit more than a few suggestions, and its purpose is to show that the greater part of inefficient water gas operation is due to improper generator operation and that most water gas machine troubles can be traced to and corrected by a change in the operation of the generator.

In Tables I and II were tabulated the average of the most important data. It is noticeable that the generator temperature is the only consistent variable; also, as this temperature goes up, the make per run and per hour increase. The oil and coke per 1,000 are lower and at the same time the quality of the gas is

TABLE I.—TEMPERATURE OF GENERATOR VARIABLE. TESTS MADE AT STATION B ON WATER GAS GENERATOR NO. 1.

	No. 1.	No. 2.	No. 2.	No. 4.
Temp. top of generator	920° C.	997° C.	1,101° C.	1,193° C.
Temp. center of carburetor.....	669° C.	566° C.	730° C.	680° C.
Temp. center of superheater.....	486° C.	591° C.	480° C.	543° C.
Blast	18.25 ins.	17.75 ins.	18 in.	18.5 in.
Steam, pounds per sq. in.....	30 lbs.	30 lbs.	30 lbs.	30 lbs.
Oil per minute.....	10.83 gals.	10.83 gals.	10.83 gals.	10.83 gals.
Oil per 1,000 cu. ft.....	3.90 gals.	3.45 gals.	3.35 gals.	3.30 gals.
Length of run.....	6 min.	6 min.	6 min.	6 min.
Length of blow.....	5 min.	5 min.	5 min.	5 min.
Average candle power.....	19.70	21.10	21.40	21.30
Average B.T.U.'s	560	610	620	650
Make per run.....	17,000 cu. ft.	18,823 cu. ft.	18,950 cu. ft.	19,910 cu. ft.
Make per minute.....	2,834 cu. ft.	3,137 cu. ft.	3,160 cu. ft.	3,318 cu. ft.
CO ₂ in blue gas (per cent by weight) ..	15.40 per cent	15.10 per cent	11.90 per cent	7 per cent
CO in blue gas.....	68.00 per cent	70.30 per cent	71.70 per cent	72 per cent
Temp. of gen. during blow.....	890° C. to 980° C.	940° C. to 1,021° C.	1,065° C. to 1,127° C.	980° C. to 1,235° C.
Temp. of carb. during blow.....	631° C. to 825° C.	580° C. to 740° C.	566° C. to 853° C.	593° C. to 805° C.
Temp. of superheater during blow.....	488° C. to 490° C.	582° C. to 590° C.	480° C. to 482° C.	530° C. to 512° C.
Make per day.....	820 M.	1,022 M.	1,046 M.	1,103 M.
Coke	27,370	25,370	34,985	3,160
Oil	3,200	3,660	4,505	3,640
Time for clinkering.....	60 min.	137 min.	81 min.	164 min.

Test made Oct. 23,
1906.

Test made Oct. 6,
1906.

Test made Oct. 26,
1906.

Test made Oct. 26,
1906.

TABLE II.—TEMPERATURE TOP FIRE 1,000° C. TO 1,200° C.

	15 Pounds Nozzle Pressure.	30 Pounds Nozzle Pressure.	45 Pounds Nozzle Pressure.
Generator blast	20 ins.	17¼ ins.	17 ins.
Carburetor blast	8½ ins.	7 ins.	7 ins.
Gas made per hour	72,470 cu. ft.	85,070 cu. ft.	82,110 cu. ft.
Gas made per run	13,069 cu. ft.	14,802 cu. ft.	15,341 cu. ft.
Oil used per minute	11.24 gals.	11.19 gals.	11.47 gals.
Oil per 1,000	4.62 gals.	3.88 gals.	3.47 gals.
Steam per 1,000 (estimated)	55 lbs.	68 lbs.	80 lbs.
Average length of blow	5.45 minutes	5.31 minutes	6.57 minutes
Average length of run	5.37 minutes	5.13 minutes	4.64 minutes
Average candle power	22.52 candle power	22.03 candle power	21.37 candle power
Average B.T.U.'s	630 B.T.U.'s	603 B.T.U.'s	639 B.T.U.'s
CO ₂ in blue gas (per cent by weight)	4.0 per cent	12.4 per cent	16.3 per cent
Average temperature of bottom fire	530° C.	330° C.	460° C.
Average undecomposed steam	1.44 grams, cu. ft.	7.02 grams, cu. ft.	15.04 grams, cu. ft.
Number of glass with opt. pyrometer			
(a) Carburetor	7	22	17
(b) Bottom of superheater	14	16	15
Coke per 1,000	41.5 lbs.	37.9 lbs.	42.7 lbs.

better. Therefore, up to a reasonable limit, the temperature of the generator is the controlling factor, with regard to resulting efficiency.

Some time ago it was necessary to burn coke that made a hot fire and no clinker, but forming large quantities of loose ash. The make per hour, right after cleaning fire, was good, but soon dropped so low that it did not pay to operate machine; 75 per cent of the combustion was taking place in the generator and only 31 per cent of the coke was going into the gas. After trying different conditions of blast and steam, the machine was clinkered every 10 hours. The result was a 22 per cent increase in make per hour for the 24 hours; a 20 per cent decrease in the coke; a 27 per cent decrease in the oil; this with an increase of 3 candle power and 10 B. T. U. in the finished gas.

Table II carries a tabulation of data secured from three different tests on an 11 ft. 6 Lowe type water gas machine with varying steam pressure. It is submitted for reference only. It is valuable in that it shows the amount of steam used in the generator should be subjected to close adjustment. The quality of the gas, as well as the make, suffers when too much or too little steam is used. On one of these steam runs (not tabulated) the excess water was over 200 pounds per run. This is easily checked by passing the gas through a weighed tube of calcium chloride, using an experimental meter to measure the gas and weighing the tube at the end of the test. This excess water has considerable to do with the boiler fuel per 1,000. Finally, although the data submitted has been carefully prepared, and in most cases the analytical work checked, it is most valuable as a means of comparison by indicating what results different conditions will produce. It must be remembered that every water gas machine is a working unit, differing in many ways from every other water gas machine in operation. In the same manner it may be said that every water gas operator is a variable that must be studied and analyzed.

If this paper has interested you to the extent of checking some or all of this data at your own plants, and using your results as a means of control, then it has accomplished its purpose.

AN EFFICIENT ELECTRIC FURNACE FOR HIGH TEMPERATURES.

By D. F. CALHANE and E. E. BARD.

A small electric furnace which gave efficient results was described in the October, 1910, issue of *Metalurgical and Chemical Engineering*. So much interest was shown in the furnace that it was decided to make it convenient for general use, and accordingly during the past year and a half a great deal of work and investigation has been done with this end in view. The furnace as finally completed is described as follows by Mr. D. C. Calhane and E. E. Bard in the August, 1912, issue of the above mentioned journal:

In the first place it was necessary to build the furnace in a way that would permit of easy assembling and dissembling.

Secondly, the use of refractories that would stand the exceedingly high temperature desired, in presence of incandescent carbon.

Thirdly, an electrical design that would give even distribution of current in the carbon core and sufficient resistance in the heating element to permit of using the furnace on the 110-volt circuit without transformers.

In what follows it will be shown how far these requirements have been met in the present form of the furnace.

The furnace is 2 ft. long, 11½ in. wide and 33 in. extreme height.

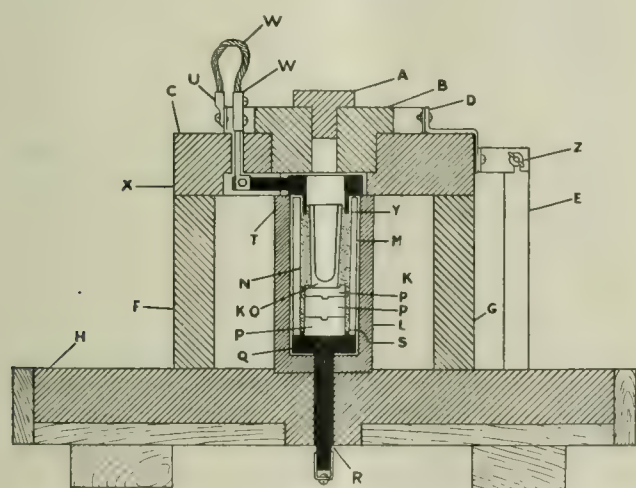
In pursuance of the idea to make the furnace in such a form as to allow of quick and easy assembling and dissembling of the parts, it has been built upon a base *H* of cement composition, contained in a wooden frame *I* that rests upon wooden blocks *J*, allowing ready access to the electrode stem *R*. After considerable experimentation to find a composition that would have both good heat insulating qualities and a certain degree of strength necessary, a mixture of sand, Portland cement and magnesia-asbestos was decided upon. *E G* to fill the base mold *I*—7.45 kg. sand, 3.75 kg. cement and 1.25 kg. magnesia-asbestos were used. These were mixed dry and the 6.0 kg. of water were

used to convert the mass to a thick paste. This was placed in the mold *I* and allowed to set. Provision was made for a hole through the mass to permit of the insertion of the electrode stem *R*.

Upon this base stand four cement sides; the two longer ones shown in vertical section at *F* and *G*. Two end pieces not there shown. These sides are cast in simple wooden boxes, painted in order to prevent warping. The inner dimensions of side boxes are 12 in. x $6\frac{7}{8}$ in. x $1\frac{5}{8}$ in.—giving a volume of 134 cu. in. each, or 268 cu. in. for the two long sides. The inside of the moulds is greased with vaselin to permit of the removal of the casts. The mixture for these two sides is sand 4 kg., cement 1.6 kg., magnesia-asbestos .6 kg., water 3 kg. The moulds are put together with screws to allow of easy dissembling of the sides and removal of the casts.

The end pieces are cast in wooden moulds whose inside measurements are $7\frac{1}{2}$ in. x $6\frac{7}{8}$ in. x $1\frac{5}{8}$ in., giving for the two a volume of 168 cu. in., requiring sand $2\frac{1}{2}$ kg., cement .8 kg., asbestos-magnesia 35 kg. and water 2 kg.

The four sides stand upon the base and are held firmly together by two iron straps and binding screws,



Section of Furnace Showing Top Ring.

forming a rectangular space, the center of which is occupied by the fire-clay muffle *L*. This is made from two No. 40 furnace muffles manufactured by the Buffalo Dental Co., of Buffalo. The space *K-K* outside the muffle and within the walls is filled with shredded asbestos-magnesia for heat insulation.

The top *C* is also of cement mixture with three holes for the top electrode connections, and a large central hole for the cover *b*. This is cast in a wooden mold designed to give the proper contour to the cast. To fill the volume of 290 cu. in. a mixture of 4.5 kg. sand, 2 kg. cement, .75 kg. asbestos-magnesia and 3.3 kg. water are used.

In the central hole of the top, fits the corner *b*, that has a different composition owing to the higher heat it is to stand. The mixture used is sand 200 gr., ce-

ment 300 gr., asbestos-magnesia 300 gr., water 850 gr., and fireclay 200 gr.

In the central hole of the cover is a cement plug *a* cast from a mixture of 40 gr. sand, 30 gr. cement, 20 gr. old fire-clay, 10 gr. new fire-clay, 40 gr. asbestos-magnesia and 100 gr. of water. All the sand used in these mixes passes 20 mesh screen. These castings as well as the top of the base, when completely dry, are given a heavy coat of water white for a finish.

Between the top *C* and the sides is placed an asbestos cloth gasket to help exclude air. Around the outside at the juncture of top with sides at *x* is fitted an asbestos cloth gasket sewed into one piece. This is bound air tight by four iron straps with tightening screws and rods, provided with thumb nuts. It is necessary to exclude air that will burn the carbon if allowed to enter.

By this arrangement it may be seen that the first requirement to make the furnace in a shape readily assembled and dissembled, has been met. Only seven cement parts have to be handled and these are put together and taken down in a very few minutes. Any one can make the moulds and cast these pieces with very little trouble.

Coming to the second requirement, the use of refractories that would stand the excessively high temperatures desired in presence of glowing carbon, the most difficult part of the problem was met. A great deal of experimentation has been done in the past twenty months and finally with the help of the Norton Company a line of alundum refractories has been developed that gives good satisfaction. The conditions are severe and put the alundum to very extreme tests. The alundum question is the backbone of the whole thing, and its wonderful properties make the furnace possible.

By reference to the cross-section figure it may be seen that the refractory portions consist of the crucible *O* that sets on three blocks *P, P, P*. The crucible is of pressed alundum $3\frac{1}{4}$ in. long, $1\frac{3}{8}$ in. wide at top and $1\frac{1}{8}$ in. wide at the bottom. It is $2\frac{3}{4}$ in. deep and will hold about 100 grams of molten steel of specific gravity 7.9. The three blocks *P, P, P*, are of tamped alundum of a special composition, to resist the excessive temperature at this part of the furnace. They are $1\frac{1}{2}$ in. wide and $\frac{1}{2}$ in. and $\frac{3}{4}$ in. thick. They are made in three sections to prevent cracking from unequal expansion.

Between the walls of the muffle *L* and the carbon core *N* is a tube of alundum *M* in two pieces 2 in. and $3\frac{3}{8}$ in. long, respectively. This arrangement, in two pieces, is to avoid cracking from uneven stresses. The walls are $\frac{5}{16}$ in. thick and bore is $1\frac{1}{8}$ in. Another crucible of alundum is also used for certain work that is $5\frac{1}{4}$ in. long and $1\frac{1}{4}$ in. internal diameter. This sets on a block $\frac{3}{4}$ in. high.

These alundum parts stand excessive heat in contact with glowing carbon. The alundum parts formed of material compacted under hydraulic pressure give

the ideal substance that is practically unaffected by incandescent carbon at 1,900° C. It has taken months of investigation to determine the best composition and size of the various alundum parts now used in the furnace.

The third proposition, the electrical design, has been a difficult one. This for two reasons: In the first place it has been exceedingly hard to obtain even current distribution in the carbon core. Any inequality in this respect results in uneven heating of the alundum that causes cracking and at the higher ranges of temperature in burning out of the alundum by carbide formation. Again, it has been difficult to design the parts for current introduction and distribution, so as to make them simple, rugged and effective in operation. It has also been necessary to design the electrical part so as to get voltage drop enough across the furnace to work it direct on the 110-volt lighting circuit without transformer and only a simple rheostat to regulate the current. This has been obtained by a long thin core of carbon, whose wattage density has had to be nicely adjusted so as not to exceed the endurance of the alundum parts at any point. After a great deal of experimentation and many changes in the electrical design success in this direction has been attained.

Referring again to the figures, p. 461, the current enters by *R*, the lead screwed into the electrode *Q* that rests on the bottom of the muffle. On the upper face of this is cut a circular lip *S*. In the inner space fit the blocks *P*, *P*, *P*, and down over the outer edge of the lip sets the alundum tube *M*. By this arrangement the current is evenly distributed all around from the upper face of the lip and through the carbon core *N* to the under side of the lip of the upper electrode *Y*. The means of exit from the upper electrode to the circuit is readily seen by an inspection of the drawing and general view of the furnace.

The voltage drop across the furnace can be varied within a range of 20 per cent by method of compacting carbon core *N* and the pressure exerted by the lip of the upper electrode on the carbon. This should be enough to give good contact, but undue pressure avoided. As an average of 10 heats, 80 volts across the furnace at 12½ amp. gave a kilowatt consumption of energy at full heat, melting point of platinum.

A block of fireclay with a hole in the center is placed upon the crucible to conserve the heat. The furnace should not be held at platinum temperature more than twenty minutes or half an hour, as the alundum does not endure so well. Alundum softens between 2,000° C. and 2,100° C. It is best to run the heat up to the m.p. of platinum as quickly as advisable and then pour the melt at once. The temperature of molten platinum is close to 1,775° C. and the hottest parts of the furnace, especially the two upper alundum blocks, are very near 2,000° C. when the crucible holds melted platinum.

As a typical instance of the working of the furnace the data from a platinum heat are appended:

Time.	Amperes.	Volts.	Watts.	Temperature, Room Temp. at start.
3.21	8.5	60	510	
3.26	8.5	45	382	
3.38	10	45	450	dull red.
3.52	12	47	564	bright red.
4.02	16.5	53	874	
4.11	19	58	1102	white hot.
4.35	15.5	66	1022	
4.38	15	70	1050	platinum melts.

Twenty grams of platinum were melted in the above heat in an hour and 17 minutes, starting with the furnace at room temperature. Starting with the furnace warm from a previous heat, the same result as above was secured in one hour. With successive heats to melting point of platinum the crucible of pressed alundum endures very well. As many as twelve successive heats to platinum m.p. have not caused any marked effect on the material of the crucible.

Alundum tube *M* sustains the extreme temperatures very well, and will endure a number of successive heats to m.p. platinum without any appreciable deterioration. Its composition is of tamped alundum with low binder.

The two top blocks, *P*, *P*, *P*, have to endure extreme temperatures and will be made in the future of hydraulically pressed alundum, done in a steel mould. This material, as mentioned in the case of the crucible, is the ideal refractory.

The design here presented is the form most convenient for melting small amounts of very high fusing metals that can be done without carbon contamination and with good electrical efficiency. Other uses require slight modifications to fit the exigencies of the case.

The adaptation of this furnace to various uses is being studied in this laboratory and a larger size along the same lines, of 6 to 7 kw. capacity, is being developed to give continuous operation. Patents are pending on the design here presented.

In conclusion, I wish to express my obligations to the Norton Co. for their kindness in developing the alundum parts; also to Mr. P. A. Boeck of the same company for valuable assistance with the alundum question; also to Mr. Bard for his valuable suggestions that have led to marked improvements in the furnace design.

An international rubber exposition will be held in Batavia, Java, from April 6 to May 9, 1914, and will embrace the discussion of such subjects as the cultivation and preparation of rubber in the principal producing regions, a review of the various species of wild rubber, and, if it can be arranged, the actual operations will be shown in order to give an idea of how rubber is prepared. The jury will be international. All requests for space from those who wish to make exhibits should be addressed to the Chairman of the Exposition Committee, Batavia, prior to July 1, 1913.

THE PURIFICATION OF TANNERY EFFLUENTS*.

Some interesting experiments have been carried out by Messrs. Hein, Faure-Fremiet, Herbert, Moussee, Sarbory and Schöffer, on the purification of tannery effluents. The experiments were made with a soak water containing a large amount of organic matter and a sodium sulphide solution used for unhairing. The results obtained by various methods of purification are given below.

PURIFICATION BY MECHANICAL MEANS.

The effluent of the water used for soaking was allowed to stand for five to six hours, the greater part of the solid matter of a granular and gelatinous nature was thus deposited, colloidal substances being left in the liquid. The amount of deposit thus obtained amounted to not more than 250 grammes in the dry state per 1,000 liters of the liquor. It was found that although little purification was brought about by mere settling, the liquor could be rapidly clarified by thoroughly mixing the liquor with water containing clay in suspension.

Similar results were obtained with the unhairing solution containing sodium sulphide, the amount of deposit obtained by settling in this case being about 1,250 grams in the dry state per 1,000 liters. The process of Messrs. Michoëlis and Rona for precipitation of albuminoids in alkaline solution was also utilized. For practical use a mixture of colophany, denatured methyl alcohol and water is recommended instead of the mastic and ethyl alcohol emulsion, which is too expensive. Investigations have been made, and are almost complete, on the conditions under which colloidal sulphur is precipitated by this method and the industrial use of the sulphur so obtained.

PHYSICO-CHEMICAL CLARIFICATION.

In this method substances were used which produce coagulation, and thus bring about a more rapid deposition of impurities. Among the various materials which can be used for this purpose, lime, ferric sulphate and aluminum sulphate were tested. In alkaline solution, aluminum sulphate gives the most voluminous and gelatinous precipitate, and is therefore expected to bring about a better and quicker deposition. When using ferric sulphate and aluminum sulphate, precipitation was therefore accelerated by making the water slightly alkaline with lime.

The quantity of reagents necessary to produce clarification of soak water is about 0.5 to 1 kilogram per 1,000 liters of soak liquor.

When lime alone was used the water was colorless and odorless; with sulphate of iron and aluminum, the odor was greatly decreased and the purified liquid perfectly limpid and fluid. When lime was employed as the clarifying agent, the purified effluent was slightly alkaline, and in the other cases it was slightly acid.

With lime and aluminum sulphate, the organic matter in the soak liquor was reduced to about half the amount originally present. The total nitrogen was reduced from 0.092 gram to from 0.033 to 0.070 gram per liter; ammoniacal nitrogen was reduced from 0.012 gram to from 0.005 to 0.008 gram per liter; sulphuretted hydrogen was completely removed, and fatty matters present were also decreased. From the chemical point of view, therefore, the purification is relatively satisfactory, especially with lime and aluminum sulphate. Ferric sulphate was not found so efficient as aluminum sulphate. The quantity used was $\frac{1}{2}$ kilogram per 1,000 liters.

With regard to physical properties, it was found that when ferric sulphate was employed the electrical conductivity of the effluent diminished from 28.88×10^4 to 19.45×10^4 ; with aluminum sulphate the conductivity was found to increase to 51.98×10^4 , due to the slight acidity acquired by the liquid. When lime was employed as the clarifying agent the conductivity increased to 78.52×10^4 on account of the small percentage of lime dissolved in the water.

The number of germs per cubic centimeter of the water was reduced from 2,000,000 originally present in the soak liquor to 4,000 in the purified effluent when ferric sulphate was used. When lime was employed, the number of germs per cc. was diminished to 71,000, and with aluminum sulphate as the purifying agent, the number of germs in the purified effluent was 81,000.

The deposit obtained from the soak liquor by the above methods of clarification was weighed, dried and analyzed in order to determine its value as a fertilizing agent for agricultural purposes. The following results were obtained per 1,000 liters of soak liquor effluent:

	Lime, grams.	Aluminum sulphate, grams.	Ferric sulphate, grams.
Dry deposit obtained.....	150.0	150.0	626.0
Nitrogen	1.41	0.63	3.15
Phosphoric acid.....	0.54	0.15	13.29
Lime	421.80	0.30	2.45
Potash	3.15	1.33	4.38

The results show that where sufficient space is available to drain off and dry the slime deposited from the effluent, some profit might be derived from its use as a fertilizing agent.

With the sodium sulphide solution used for unhairing, similar results were obtained by use of the above compounds for clarifying the effluent, lime, however, being an exception. When lime was used, the clarified liquor was yellowish in appearance, almost odorless and very alkaline. The total nitrogen was decreased from 1.000 grams to 0.008 grams per liter; the ammoniacal nitrogen from 0.081 to 0.013 grams per liter; fatty matters were decreased. The effluent was thus greatly improved, but the clarified liquor always contained large amounts of sulphuretted hydrogen, the amount remaining practically constant.

When lime was employed, the number of bacteria was reduced from 500,000 to 81,000 per c.c., and the

*From the Leather World, 4, 119-20 and 144-5.

deposit on analysis gave the following results per 1,000 liters of the effluent:

	Grams.
Dry deposit.....	22,500.0
Nitrogen.....	31.5
Phosphoric acid.....	2.25
Lime.....	8,721.0
Potash.....	128.25

From the amount of fertilizing elements thus present this deposit should be worth collecting and drying for use on the soil.

PURIFICATION BY CHEMICAL REACTIONS.

This method differs from those given above in that substances were used which react chemically on the impurities present in the water. The reagents tested for this purpose were: (1) A mixture of ferric sulphate and chloride of lime; (2) calcium permanganate; (3) sodium hypochlorite.

These reagents were added to the effluent until no further precipitation took place and until the odor of the soak water was removed. The quantity of reagents employed per 1,000 liters of effluent was as follows:

	Grams.
Ferric sulphate.....	250
Chloride of lime.....	200
Permanganate of lime.....	100
Sodium hypochlorite.....	3,000

The soak liquor, after treatment with the above reagents, was allowed to stand for a few hours to allow the precipitate to deposit. The clear solution thus obtained was slightly yellow in color, the putrefactive smell was greatly diminished. When reagents (1) and (3) were used, the smell of the purified liquor resembled that of chlorine.

The purified effluent was slightly acid when ferric sulphate and chloride of lime were employed, neutral when calcium permanganate was used, and slightly alkaline when the precipitating reagent was sodium hypochlorite.

With reagents (1) and (2) the organic matter present was decreased, but this was not estimated when sodium hypochlorite was employed. Total nitrogen was reduced from 0.075 gram per liter to 0.56 and 0.067 gram per liter respectively when the first two reagents were employed. With sodium hypochlorite the total nitrogen was reduced from 0.092 gram to 0.078 gram per liter. The amount of ammonia was diminished considerably with the two first reagents, and practically completely removed with sodium hypochlorite. Sulphuretted hydrogen was reduced and fatty matters were decreased.

Ferric sulphate and chloride of lime reduced the number of germs originally present in the soak water to 640 per c.c. With calcium permanganate, purification in this respect was greater and sterilization was complete.

Sodium hypochlorite charges the water with chlorinated compounds, renders it alkaline, and reduces the number of germs to 8,500 per c.c.

Though purification is satisfactory when the above chemical reactions are employed, the result was found to be inferior to that obtained with the clarifying

agents previously mentioned, especially with lime.

The following analysis of the deposit obtained when the three chemical reagents given were used shows that it possesses little fertilizing value.

	Ferric sulphate and chloride of lime, grams.	Calcium permanganate, grams.	Sodium hypochlorite, grams.
Dry deposit obtained	85.00	123.00	400.00
Nitrogen.....	0.23	0.27	3.25
Phosphoric acid....	2.78	0.39	0.26
Lime.....	3.07	6.88	0.52
Potash.....	2.04	1.47	0.88

The quantities given are per 1,000 liters of liquor.

With the sodium sulphide effluent used for unhairing, the following reagents were used: Ferric sulphate, alumina sulphate, mixtures of 5 parts ferric sulphate and 2 parts chloride of lime, calcium permanganate and sodium hypochlorite.

These reagents were all found to considerably improve the appearance of the effluent, especially ferric sulphate, alumina sulphate, and calcium permanganate, but the purified effluent still contained a considerable amount of sulphuretted hydrogen. The best results seemed to be given with ferric sulphate, which is also cheaper.

With these reagents the viscosity of the effluent was greatly decreased, especially when ferric sulphate was employed. The calcium permanganate and mixture of ferric sulphate and chloride of lime reduced the surface tension of the effluent to the greatest extent, though in all cases it was decreased. The variation of these physical constants is worthy of note, considering the great alkalinity of the purified effluent.

The use of ferric sulphate decreases the number of germs to 5,000 per c.c.; with ferric sulphate and chloride of lime in admixture the number of germs were reduced to 1,500 per c.c.; sodium hypochlorite diminished them to 7,200; and aluminum sulphate to 49,000; while calcium permanganate completely sterilizes the water.

On analysis of the deposits the following results were obtained, quantities referring to 1,000 liters of effluent:

	Ferric sulphate, kilograms.	Aluminum sulphate, kilograms.	Ferric sulphate and chloride of lime, kilograms.	Calcium permanganate, kilograms.	Sodium hypochlorite, kilograms.
Dry deposit obtained....	10.50	33.05	3.87	4.04	3.50
Nitrogen.....	38.43	78.40	8.67	7.92	43.40
Phosphoric acid.....	11.65	1.92	7.66	11.31	0.87
Lime.....	282.20	78.40	582.32	743.36	5.25
Potash.....	30.45	188.65	69.93	64.46	104.30

These deposits should be of value as fertilizing agents.

From the experiments thus carried out, Mr. Heim concludes that though the water is considerably improved, except as regards amount of sulphuretted hydrogen present, the cost of the process for this result is too great unless the deposit could be satisfactorily

utilized. In order to compensate further for the expense of purification, experiments have been, and are still being, carried out in order to recover the sulphur from the effluent. This would be very valuable as a by-product.

Two methods for this purpose have been tested by Mr. Heim. Using the method with mastic, already referred to, a light yellow water was obtained possessing a smell of resin, quite fluid and slightly acid. The total nitrogen was reduced from 1.960 grams to 0.728 gram; ammoniacal nitrogen from 0.084 gram to 0.068 gram; and sulphuretted hydrogen from 10.241 grams to 1.423 grams per liter.

The second process investigated consisted in agitating the effluent with clay, afterwards acidifying with sulphuric acid, then filtering or decanting off the clear solution.

A light yellow acid solution, smelling slightly of sulphuretted hydrogen, was thus obtained. The total nitrogen was decreased from 1.96 to 0.56 gram; ammoniacal nitrogen from 0.81 to 0.065 gram; and sulphuretted hydrogen from 10.241 grams to 0.758 gram per liter. The number of germs was greatly reduced. A considerable amount of sulphuretted hydrogen was liberated during the process, the sulphur from which could be recovered by processes similar to those employed for purifying coal gas. The effluent also, after purification, grows more and more turbid, due to the deposition of colloidal sulphur. This can be coagulated with lime and then collected. Experiments are being made on the sulphur thus recovered with a view to employing it for making mixtures for use in agriculture.

BIOLOGICAL PURIFICATION.

From experiments made in the purification of soak liquor, Mr. Heim concluded that, leaving out of account the relative cost of the different processes, it was impossible to obtain sufficient purification by the aid of aerobic or anaerobic organisms without extending the work to an extent which would not be practical in this industry. Purification by direct filtration on bacteria contact beds, and also by filtration after fermentation, is very satisfactory from a bacteriological point of view, but is much less satisfactory with regard to chemical composition. If the septic tank is first employed, a considerable decrease in organic matter is then obtained on the bacteria beds. This is not the case if the effluent is conveyed directly into the bacteria beds. In both cases, however, the total ammoniacal nitrogen is not decreased to any considerable degree. Taking into account the chemical composition of the effluent before and after, as well as the number of germs present, the results obtained by biological methods of purification were inferior to those obtained by chemical purification.

The declared exports of Chicle gum from Yucatan ports to the United States during the first quarter of 1912 were as follows: Campeche, \$164,043; Ciudad del Carmen, \$47,151, and Progreso, \$29,106.

USE OF COPPER SALTS IN GREENING OF FOODS.

The question of the use of copper salts in the greening of foods was referred by the Secretary of Agriculture, on March 11, 1909, to the Referee Board of Consulting Scientific Experts. Exhaustive investigations have been conducted by that board, and the Department of Agriculture has received the report of the investigations. The questions which were referred to the Referee Board are as follows:

"Are vegetables green with copper salts adulterated under the Food and Drug Act of June 30, 1906, because (a) a substance has been mixed or packed with them so as to reduce or lower or injuriously affect their quality or strength; (b) they have been mixed, colored, powdered, coated, or stained in a manner whereby damage or inferiority is concealed; (c) they contain any added poisonous or other added deleterious ingredient which may render such articles injurious to health? (1) in large quantities? (2) in small quantities?"

The main general conclusions reached by the Referee Board from a study of their experimental results and other considerations are as follows:

(a) Copper salts used in the coloring of vegetables, as in commercial practice, can not be said to reduce or lower or injuriously affect the quality or strength of such vegetables as far as the food value is concerned;

(b) Copper salts use in the greening of vegetables may have the effect of concealing inferiority, inasmuch as the bright green color imparted to the vegetables stimulates a state of freshness they may not have possessed before treatment;

(c) In attempting to define a large daily quantity of copper regard must be had to the maximum amount of greened vegetables which might be consumed daily. A daily dose of 100 grams of coppered peas or beans, which are the most highly colored vegetables in the market, would not ordinarily contain more than 100 to 150 milligrams of copper. Such a bulk of greened vegetables is so large, however, that it would hardly be chosen as part of a diet for many days in succession. Any amount of copper above 150 milligrams daily may, therefore, be considered excessive in practice. A small quantity is that amount which in the ordinary use of vegetables may be consumed over longer periods. From this point of view 10 to 12 milligrams of copper may be regarded as the upper limit of a small quantity.

It appears from our investigations that, in certain directions, even such small quantities of copper may have a deleterious action and must be considered injurious to health.

The Food and Drugs Act of June 30, 1906, provides that a food is adulterated "if it contain any added poisonous or other added deleterious ingredient which may render such article injurious to health." The act also provides that a food is adulterated "if it be * * * colored * * * in a manner whereby damage or inferiority is concealed." It is apparent from the findings of the Referee Board that all foods greened with copper salts are positively adulterated under the first above-quoted provision of the law, and that in certain cases foods may be adulterated under the second above-quoted provision.

The complete report of the investigations and conclusions of the Referee Board on this subject will be published by the Department of Agriculture.

METALLURGY

PROBLEMS IN ACTUAL WORK PRACTICE IN THE METALLURGY OF STEEL.

An interesting paper, dealing with some problems that have arisen in actual works practice, in connection with the metallurgy of steel, and the methods that were used in solving them, was presented recently before the Detroit Society of Chemists by Mr. Wm. D. Mainwaring, chemist and metallographist. In his paper Mr. Mainwaring illustrates the phenomena of segregation and the methods of sampling the steel in question from a manufacturer's and consumer's standpoint; the effect of size and temperature of rolled bars and the effects of cold work on the physical condition of steel; also the effects of improper annealing on the structure and strength of test bars from cast steel. It also illustrates how the manufacturers of machinery and other articles made from steel or iron, who do not have the facilities for producing the castings or forgings that are component parts of the completed machine, are sometimes at the mercy of unscrupulous dealers in these products.

Mr. Mainwaring's paper contains so much matter of interest to the factory metallurgist that we are abstracting it as follows:

The first problem will deal principally with the segregation of sulphur in Bessemer steel and the different results obtained by the various methods used in sampling the steel. Segregation is defined as the concentration of the more fusible parts of the steel into local centers, which are the last to cool. As the molten steel from the ladle comes in contact with the cold sides of the ingot mold, an outside layer or envelope forms, which is practically of the same analysis in all parts of the layer. As the metal inside this layer cools, crystallites purer than the residual liquid fall out of solution. The remaining mother liquid gradually becomes more impure and of a lower melting point and specific gravity than the rest of the solidified metal, and therefore rises to the top of the ingot.

It might be asked here, Why does not the steel cool in graduated layers of a different composition? The reasons are two: First, the descending current of purer crystalites, as they freeze, landlocks portions of the ascending current of the impure mother liquid. The second reason is that, as all steels and iron have an affinity for carbon, sulphur, etc., the impurities partly diffuse out of the mother liquid into the purer crystallites during and after imprisonment, and it is only a small part of the mother liquid that finally finds its way to the top of the ingot.

TABLE I.—SULPHUR ANALYSIS.

Car. No.	Billet No.	Sulphur.	Car. No.	Billet No.	Sulphur.
1104	1	0.132	3978	1	0.112
1104	2	0.070	3978	2	0.125
1104	3	0.072	3978	3	0.112
1104	4	0.100	3978	4	0.040
3385	1	0.150	4927	1	0.160
3385	2	0.153	4927	2	0.120
3385	3	0.160	4927	3	0.093
3385	4	0.087	4927	4	0.100
Car. No.	Billet No.	Sulphur.	Car. No.	Billet No.	Sulphur.
5194	1	0.143	52632	1	0.169
5194	2	0.130	52632	2	0.168
5194	3	0.115	52632	3	0.091
5194	4	0.115	52632	4	0.069
43487	1	0.133	5581	1	0.123
43487	2	0.090	5581	2	0.155
43487	3	0.081	5581	3	0.169
43487	4	0.119	5581	4	0.198

Note.—Car 5581 previously rejected and ordered shipped back without dispute, on receipt of drillings from these four billets.

That segregation occurs in two ways, namely, from bottom to top and from outside to center, the following will clearly show: The Bessemer steel in question was received in the early part of 1905 from one of the large producers and was intended for welding purposes, as prior to this time very little welding was being done by the electric process. As this came into vogue it was discovered that this class of steel was not suited to electric welding, on account of its great tendency to crystallize under this treatment, and its use was finally discontinued. On analysis it was found that several of the carloads were running abnormally high in sulphur. This class of steel is considered in carload lots, two or three billets being selected from the car for analysis. As soon as this was discovered the different blow numbers were looked for, as it seemed to be a case of stuffing the ballot box as well as of intense segregation. Table I shows results of analysis of sulphur first obtained by the regular practice of sampling the steel.

A few of the billets drilled on opposite ends proved that intense segregation of sulphur was present. These results are shown in Table II, which illustrates segregation of sulphur.

TABLE II.—SULPHUR SEGREGATION.

Car No.	Billet.	First End Drilled.	Opposite End.
3385	No. 2	0.153	0.075
5194	No. 4	0.115	0.120
43487	No. 4	0.119	0.084
52632	No. 1	0.169	0.160
3978	No. 2	0.125	0.106

The matter was immediately referred to the manufacturers, who sent their representative to the works. He made the claim that the method used in sampling the steel was entirely wrong, stating that they (the manufacturers) had examined the four drilled billets from car No. 5581, taking planings from the outside longitudinally to a depth of $\frac{1}{2}$ in., and found a sulphur content of not over 0.060 and that the steel in

question should be drilled from the outside, going to a depth of $\frac{1}{2}$ in.

The superintendent of the plant being away at the time, the expert was referred to the author, who was instructed from the office to follow out the method of sampling as suggested by him, and it was done under protest. One billet was selected from each car, the billets chosen being those that had previously been drilled, with the exception of those from car No. 4927. These billets having been covered up, a new billet was selected. The billets were drilled on opposite ends to those previously drilled, using the method stated. Table III shows the comparison of results on billets selected with those previously obtained.

TABLE III.—SULPHUR SHOWING BY DIFFERENT SAMPLING METHODS.

Car. No.	Billet No.	Author's Method.	Expert's Method.
1104	2	0.132	0.083
3385	2	0.153	0.058
3978	2	0.125	0.056
4927	New Billet	None	0.051
5194	4	0.115	0.050
43487	4	0.119	0.053
52632	1	0.169	0.080

On the return of the superintendent, the question was taken up very vigorously, the claim being made that the method of drilling billets used was very favorable to the steel company, which was supported by results of analysis obtained from drillings taken by the author's method on the same ends of billets drilled for the steel expert and also from side to side to center. It was stated that if billets were drilled on the side, the drilling should continue through the billet, but not being able to do this, a compromise was made by going one-half through. Table IV shows a comparison of results obtained by the regular practice of drilling and by the expert's method and by drilling from center to side.

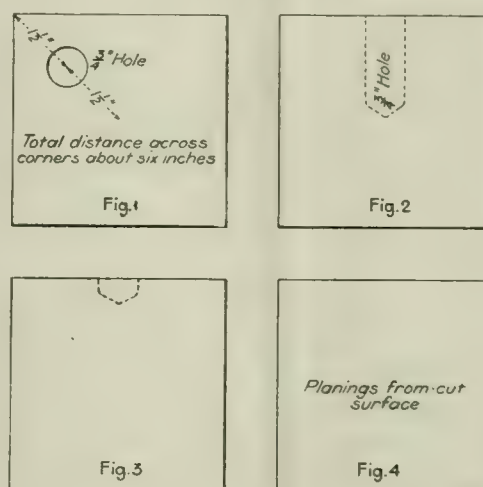
TABLE IV.—FURTHER COMPARISON OF DIFFERENT SAMPLING METHODS.

Car No.	Billet.	Regular Practice.	Expert's Method.	Side to Center.	Planings from Cut Surface
3385	No. 2	0.153	0.058	0.150	0.085
5194	No. 4	0.115	0.050	0.118	0.085
43487	No. 4	0.119	0.053	0.117	
52632	No. 1	0.169	0.080	0.150	0.132

The question was again taken up with the steel company, which requested new drillings. Part of the drillings from side to center were furnished. On making analysis, they again sent their representative, and after consultation with the superintendent and the author, it was decided to select three of the billets drilled from side to center, to cut them in two, to plane this cut parallel with sides and then to take planings from this cut surface. These were mixed thoroughly and divided into two parts, one to be analyzed for the works and the other by the steel company. It was agreed that if any of the analyses showed over 0.080 per cent sulphur, which the specifications for this steel called for, all cars in dispute would be ordered shipped back. The results of the analyses are given in the last column of Table IV.

It would seem that billet No. 2 of car No. 3385 was cut in two on the low sulphur end, this billet and No. 4 of car No. 43457 having been shown in Table II to be very badly segregated and indicating that a higher result would have been obtained if the billet had been cut on the opposite side. An average of the results obtained from the two ends of this billet and of the result obtained by drilling from the side to a depth of $\frac{1}{2}$ in. gives the sulphur content as 0.086 per cent. Assuming no sulphur on the extreme outside surface of billets, and taking the average of this and the results obtained by the regular method of drilling billets, shows that a result very favorable to the steel company is obtained by drilling or planing billets to a depth of $\frac{1}{2}$ in. from outside.

The accompanying sketches illustrate the four methods used in sampling the billets. It should be borne in mind that it is merely an assumption that no



Sketch Showing Method of Sampling.

sulphur exists on the outside skin of these billets. Possibly the molten metal as it comes in contact with the cold sides of the mold, in the formation of the outside layer, will under certain conditions reject about one-half of the contained impurities. The results prove that a comparative result can be obtained by drilling billets as in Figs. 1 and 2; that method shown in Fig. 3 gives false results and that in Fig. 4 gives absolute results, but is too expensive and cumbersome for everyday practice where a great many billets have to be analyzed.

The second problem deals with the effect of size and temperature on the physical properties of hot rolled bars, and will particularly illustrate that if bars of steel of large and small sections are required of a certain specification as to physical strength, a much lower carbon stock should be used on the smaller sections for the reason that the bars of small size will have more work put on them than those of larger sectional area. Also, the smaller bars are very liable to be at a lower temperature at the finishing rolls than the large bars. The more work put on a bar and the colder the steel is rolled the higher will be the tensile strength. The closer the point of recalcence is

approached as the finishing temperature, the better will be the physical properties of the steel. If a series of bars of varying sizes of the same carbon stock are rolled at the same finishing temperature, it will be found that as the sectional area becomes smaller the tensile strength raises; also that if another series of bars of the same sectional area, at the finishing rolls, are rolled at varying finishing temperatures, as the final temperatures are lowered the physical strength will be increased.

The accompanying tables will illustrate these points. The bars tested were rolled from medium steel under the manufacturer's standard specifications, calling for the following physical properties: Ultimate strength, 60,000 to 70,000 pounds; elastic limit, not less than one-half the ultimate; per cent elongation, 1,400,000 divided by ultimate strength; for use for concrete reinforcing bars and inspected by the Pittsburgh Testing Laboratory.

An inspection of Series No. 1, Table V, will show that the steel was too good for the purpose intended. A considerable amount was rejected by the inspector, as it was above the specification called for, but on pointing out that the ductibility, as measured by the elongation, reduction of area and bending tests, was excellent, the steel was finally accepted by the customers.

TABLE V.—PHYSICAL PROPERTIES OF THE 0.35 CARBON STEEL BARS.

Size, ins.	Elastic limit.	Ultimate strength.	Elongation, per cent in 8 ins.	Reduction of area, per cent.
$\frac{7}{8}$	44,184	72,741	25.	47.51
$\frac{3}{4}$	47,891	73,471	26.1	51.91
$\frac{5}{8}$	59,873	79,277	25.	49.67
$\frac{3}{8}$	57,800	82,569	15.6	49.51

In the next lot of steel rolled a lower carbon stock was used, on which results shown in Table VI were obtained.

TABLE VI.—PRINCIPAL PROPERTIES OF 0.30 CARBON STEEL BARS.

Size, ins.	Elastic limit.	Ultimate strength.	Elongation, per cent in 8 ins.	Reduction of area, per cent.
$2\frac{1}{2} \times \frac{1}{2}$	40,854	62,637	25.0	44.06
1-3/16	44,140	64,910	23.4	40.40
1	35,270	67,110	22.6	46.90
$\frac{5}{8}$	43,800	70,500	24.26	35.60

Note.—There is a doubt in my mind of the accuracy of the elastic limit of the 1-in. bar. It was measured by caliper by the inspector and the beam weight noted. With the exception of the $\frac{1}{4}$ -in. rounds listed in Table VIII, this steel fulfilled the specifications called for.

In connection with this series two 4x4 in. billets of 0.28 carbon steel were rolled down to $\frac{3}{8}$ in. round. The first and last ends of the resulting bars were sheared off and marked 1 and 2 respectively, as well as the heat numbers used, and a physical test was made on the cold bars. The first end to enter the finishing rolls as viewed from its color would be about 990° C., while the last end was probably between 700 and 600° C. The results obtained were as given in Table VII.

TABLE VII.—PHYSICAL PROPERTIES OF 0.28 CARBON STOCK ROLLED INTO $\frac{3}{8}$ -IN. BARS.

Location of bar.	Elastic limit.	Ultimate strength.	Elongation, per cent in 8 in.	Reduction of area, per cent.
Heat 1505				
First end	49,000	66,500	25.0	48.25
Last end	50,800	70,140	25.	48.05
Heat 2583				
First end	52,000	69,369	23.90	48.03
Last end	54,400	71,328	21.90	48.02

It being intended to roll all the steel required to fill the orders from the same heat numbers as far as possible, in order to have the analysis uniform, the ends of the larger bars, after they had been cut to the desired length, were rerolled into the $\frac{1}{4}$ -in. bars, and it was found that they were about 5,000 pounds over the specified limit for ultimate strength. Two bars soaked in a heating furnace for 15 minutes at about 900° C. and slowly cooled in a place warmed by the heat of the furnace failed to lower this strength; in fact, one of the bars was considerably higher.

TABLE VIII.—PHYSICAL PROPERTIES OF 0.30 CARBON BARS ROLLED TO $\frac{1}{4}$ -IN. SIZE.

Bar.	Elastic limit.	Ultimate strength.	Elongation, per cent in 8 in.	Reduction of area, per cent.
Raw	50,100	75,000	23.40	49.10
Soaked in furnace 15 min.	Not taken	75,500 76,000		

It has been seen in the foregoing that the lower temperature at which the bar is finished and the more work that is put on it, the higher will be its tensile strength. If this work is carried on well below the recalcence point and tests are made at various stages of this working, it will be found that the bar will become stiffer; that is, it will have greater resistance to bending, and that finally it will not bend at all without breaking. It will fracture simply from the force of the blows directed upon it, showing that the steel has become almost as brittle as glass.

One or two years ago a customer made a complaint that some ovals received for use in making carriage and automobile tops were too stiff for the purpose intended. The discovery was made by a bending test.

In looking up the history of the ovals, it was found that all had been rolled from the same heat number. An analysis was made for carbon only, it being found, from the mill reports, that the other elements were well within the specifications for this class of steel. The 9/16x9/32-in. ovals marked hard showed 0.11 per cent carbon; those marked O. K. showed 0.12 per cent; $\frac{1}{2} \times \frac{1}{4}$ -in. bars marked hard showed 0.13 per cent carbon and those marked O. K., 0.13 per cent, showing the chemical composition was not at fault. A microscopical examination revealed the fact that the bars marked hard had been rolled too cold, as shown by the elongated condition of the component crystals of the specimens cut from them, while the bars marked O. K. showed the normal crystalline condition.

In another case a customer complained that all of the steel he was getting was hard and brittle. Three pieces were sent along to support the claim. They were about 8 in. long, one end having the original 1-in. square section, while the other had been hammered down to about $1\frac{1}{2} \times \frac{1}{8}$ in. An analysis of the three pieces showed the carbon to be 0.15 per cent; manganese 0.40 to 0.45; phosphorus, 0.035 to 0.040, these being the hardening elements, proving it to be a good grade of steel. A microscopical examination made on the flattened end showed it to be extremely

overworked. On making a bending test this end commenced to fracture after being bent to an angle of about 30 degrees.

The bar showing evidences of having been in the fire, the author concluded that it had been heated just below its recalcence point and then hammered down, the work continuing long after the bar was cold, which had made it brittle. To prove that it was not the fault of the steel, one of these hammered ends was heated in a blacksmith forge to about 950° C. and put across two iron bars to cool, which would cause it to be cooled quite rapidly. Even after this rapid cooling the piece was bent flat on itself twice without a trace of fracture, the power hammer being used to give it the final bending.

The fifth problem deals with test bars from cast steel. Last fall it came to the author's attention that an annealed test bar from cast steel had fallen down very badly in the physical test. The data of this bar were as here given. Bar as cast 1½ in. square by 14 ins. long was heated uniformly in a blacksmith forge and then covered with the burnt coals in the forge over night. The bar was then turned down to ½ in. diameter and the tensile test made.

ANALYSIS.	
Carbon	0.27
Phosphorus	0.060
Manganese	0.75
Silicon	0.29

PHYSICAL TEST.	
Ultimate strength.....	62,000 lbs. per sq. in.
Elongation.....	49 per cent in 2 ins.
Reduction of area.....	50 per cent

From these data it appeared that the bar had been overannealed, causing the pearlite and ferrite to segregate in large areas, which would give a weak structure, and the author suggested that a sample be furnished for microscopical examination.

A second bar was taken from the same blank, heated uniformly throughout, quenched in water, heated again and then annealed. It was then turned down to ½ in. diameter and a physical test made with results as follows: Ultimate strength, 74,000 pounds; elongation in 2 ins., 39 per cent; reduction in area, 40 per cent. No test bar should be treated differently from the steel it is supposed to represent is treated, in order to get a high tensile strength.

The last problem to be mentioned had to do with the breaking of the crankshaft of a single-cylinder single-valve center-crank upright engine, connected direct to a 180-kw. engine-type generator operated at 200 r.p.m. The generator rotor was mounted on a coupled extended shaft and two of the units were installed in the plant. The specifications of the engine, as furnished by the builders, was very weak as far as the crankshaft is concerned, reading as follows: Shaft will be a solid piece of open hearth steel of ample size and the crank provided with suitable cast-iron counter weights. There was an abrupt change of sections in the various parts and at one of the points where the flat section joins the round section the break occurred.

After the first engine finished had been in operation for a week and a half, the crankshaft broke while running under normal load. The author was requested to make an analysis for carbon and a test for ultimate strength on two pieces that had been machined from the broken surface. The carbon was 0.25 and the ultimate strength was 50,000 to 55,000 pounds. In the meantime the other engine had been put in commission. In one and a half weeks to a day, the crankshaft of this engine let go. An examination of the broken surface of the two shafts and a fracture made on two bars, one from the center and one from the side, machined from both of them, indicated that the shafts were castings and mighty poor ones at that. As the carbon on the second one was also 0.25, it was concluded that both of them had been cast from the same heat.

It was not until 1907, two years after the breaks occurred, that specimens were cut from the bars, one from the outside and one to represent the center, to be polished by hand and etched for study by means of a microphotograph. The structure of one of the crankshafts was compared with that of a known 0.30 carbon steel. The specimen of the center of the crankshaft was of a coarser structure than the outside, on account of its being the last to cool. The structure of a forged bar was also photographed, demonstrating still further that the shaft was a casting.

According to an announcement of the U. S. Geological Survey, American mines in 1911 yielded \$2,750 worth of diamonds, \$9,500 worth of emeralds, \$215,313 worth of sapphires and \$44,751 worth of turquoise. The total production of gems and precious stones in the United States shows an increase over 1910, but is considerably lower than in the years 1907 to 1909, the value in 1911, as reported to the Survey and as estimated in part, having been \$343,692 against \$295,797 in 1910. The production in 1911 may be stated to have been: As reported—amethyst, \$725; beryl, aquamarine, blue, pink, etc., \$2,505; californite, \$150; chiastolite, \$25; chlorastrolite, \$1,002; feldspar, sunstone, amazon stone, etc., \$175; garnet, hyacinth, pyrope, almandine, rhodolite, \$2,005; gold quartz, \$1,700; jasper, petrified wood, bloodstone, etc., \$2,240; malachite, azurite and azurmalachite, \$800; peridot, \$360; quartz, rock crystal, smoky quartz, rutilated, etc., \$2,140; rose quartz, \$1,744; rhodonite, \$1,300; smithsonite, \$25; spodumene, kunzite, hiddenite, \$75; thomsonite, \$1,500; topaz, \$2,075; tourmaline, \$16,445; miscellaneous gems (obsidian, datolite, fossil coral, beach pebbles, pink apatite and ornamental stones with trade names), \$3,224. As estimated—agates, chalcedony, etc., moonstones, etc., onyx, \$8,128; chrysoprase, \$13,550; diamond, \$2,750; emerald, \$9,500; opal, \$1,875; ruby, \$210; sapphire, \$215,313; turquoise and matrix, \$44,751; variscite, amatrice, utablite, \$5,750.

METALLOGRAPHY AND METALLURGY AT THE BUREAU OF STANDARDS.*

By GEORGE K. BURGESS, SC. D.

Among the functions of the Bureau of Standards is the determination of physical constants and the properties of materials when such data are of great importance to scientific and manufacturing interests. Although there are innumerable physical constants and properties of materials that are not yet known with the accuracy oftentimes needed in the sciences and arts, a selection is most naturally made from among those problems for which on the one hand the need for their solution is presented in some concrete form, and on the other hand from among those problems which in themselves are evidently fundamental and form a basis for many applications.

A glance through a standard treatise such as Prof. J. W. Richards' "Metallurgical Calculations" will convince anyone of our deplorable lack of sufficiently exact knowledge of many of the constants and fundamental properties of materials necessary to a proper carrying out of many of even the more usual operations in metals alone, to say nothing of the other metallurgical products. For example, at the temperatures at which they are usually worked, for most metals we do not know either their specific heat, heat of fusion, thermal or electrical conductivity, porosity to gases, thermal expansion, mechanical properties, of which there are so many, or their radiation properties, nor for any one metal do we know all of these well enough even for a rough calculation of the efficiency of a projected new operation.

The Bureau of Standards receives almost daily requests for more exact information in this field, but cannot pretend, with its present limited staff and equipment to keep abreast even of the most urgent demands. As has been pointed out by others, the United States lags behind Europe in an aggressive attack from the scientific side, which forms the basis for all rational development, of the problems underlying the metal industries and on which their ultimate economy depends.

By studying just such fundamental problems of interest either directly or indirectly to the metallurgist, the Bureau of Standards hopes to be able in some measure to be as useful to the scientific and industrial world in general and to the metal industries of America in particular, as are the corresponding foreign national physical and testing laboratories such as those of England, France and Germany.

To cite some of the metallographic work of but one of these, the English, we may mention the comprehensive study of the iron-carbon system and of the heat treatment of high-speed steels, and more recently the mechanical properties of steel at high temperatures and a very elaborate study of aluminium alloys, some of which find application in aeronautical and naval construction.

In the field of metallography and physical metallurgy there are, of course, individuals in this and other countries who are working independently and producing admirable results; nevertheless many urgent problems require complicated and costly equipment, and others are so elaborate that the association of a group of persons becomes imperative for a complete solution within a reasonable time of all the phases involved; and such cases fall naturally to the lot of the laboratory which has facilities for attacking simultaneously the various aspects of the problem such as physical, chemical, metallographical and mechanical, and on a scale, when necessary, of sufficient magnitude involving large units to work with, that an individual would in most cases not care to consider.

The testing and research laboratories of some of the larger manufacturers also produce, oftentimes, results of the greatest scientific interest and practical importance, but usually they are mainly interested in attaining some definite technical goal, so that their general work, when available, requires supplementing and generalizing to make it most useful. This is particularly true for investigations of the metals and their alloys; the temptation for a commercial laboratory to discontinue an investigation when a given material having the sought-for properties is attained is too great to be resisted. For example, an electrical firm seeking a high resistance, high melting-point alloy of small temperature coefficient, will probably drop the problem when a suitable alloy is found, regardless of other equally valuable (to someone else perhaps) properties that may have shown signs of developing during the research.

For all those reasons it is clear that a national physical and materials laboratory has a very definite role assigned to it in its relation to the progress of metallurgical science on the one hand and to the metallurgical industries on the other.

The question may be raised as to the respective provinces of the Bureau of Mines and the Bureau of Standards. The former occupies the domain between the Geological Survey and the Bureau of Standards, and in the words of the report of the House Committee on Mines and Mining:*

"Nothing in these provisions (i. e., the bill H. R. 17260 amending the act establishing the Bureau of Mines) would authorize or permit the Bureau of Mines to extend its investigations beyond 'mining' operations so as to duplicate the geologic and topographic work of the Geological Survey; nor will anything herein authorize the Bureau of Mines to extend its work to cover the investigation of finished manufactured products, which come properly within the scope of other branches of the government service."

Briefly, then, the Geological Survey deals with materials in the ground, the Bureau of Mines with getting them out of the ground and refinement from the ores and the Bureau of Standards with the properties

*From Metallurgical and Chemical Engineering.

*House of Representatives, 62d Congress, Report No. 243, 1912.

of the manufactured material. Another well recognized phase of the work of the Bureau of Standards is, of course, the investigation of testing methods and the certification of measuring instruments of all sorts.

The bureau has for some time been engaged on problems of interest to the metallurgist. One of the most important is the preparation and analysis of standard samples of irons, steels, alloys and ores which are distributed broadcast to works, chemists and others interested, for a small fee, and serve as a basis for obtaining uniform analytical results in all localities by checking both the metallurgical chemist and his methods. Incidentally new and better methods of analysis have been devised and described for some of these materials.

Samples of standard substances, such as naphthalene, sucrose and benzoic acid are similarly distributed for the standardization of combustion or fuel calorimeters. The preliminary study and preparation of these calorimetric combustion standards have entailed very elaborate investigations which are still in progress and in the course of which new methods and apparatus have been devised. A study of the calorimetric and thermal properties of various gases is also under way.

A very troublesome problem of the greatest practical importance, which is being investigated with thoroughness and on a large scale, is the resistance of steels to electrolytic and corrosive action. Some extremely interesting data have been obtained which will be published shortly.

The mechanical properties of the metals, especially of steels suitable for structures, have received considerable attention, although this work has been but recently organized, and with the completion of the new machines now being installed at Washington and Pittsburgh, the bureau will be equipped for testing of large members, as well as for the usual test sizes.

A comparative experimental study of the methods of determining hardness has been made, a modification of the Brinnell test suggested and several investigations on the correlation of the physical and mechanical properties of steels are under way, having as a partial object the simplification of the test.

Some of the thermal properties of the metals have been studied with particular care; for example, a considerable number of melting points have been determined with exactness for use in defining the temperature scale to 3000° C. An investigation of the reproducibility of some of these standard temperatures by means of metals from various sources has also been made, and a new method devised for the determination of the melting points of microscopic samples. A study of the methods of obtaining cooling curves has been published.

Sir Robert Hadfield has placed at our disposal several hundred samples of steel for the determination of melting and transition points, hardness, etc. These

steels, covering a very complete range of compositions, are of particular interest, as many of their mechanical, magnetic and electrical properties have already been studied elsewhere.

A thermal analysis has been made of a series of standard steels for Prof. H. M. Howe in conjunction with his thermo-microscopical study of grain size. The results of this investigation have confirmed our previous opinion of the desirability, in view of the existing confusion on many points, of attacking anew the iron-carbon series of alloys from the thermal standpoint, using only pure components, i. e., eliminating all impurities and studying one by one all the factors that enter into the location of the transition points on heating as well as on cooling, such as methods of measuring the phenomena, rate of temperature change, atmosphere, impurities, size of sample, etc., etc. Starting with pure iron, some interesting and unexpected results have been obtained which will be published shortly.

It is planned to attack in a similar way other series of alloys of practical and scientific importance, and to determine for these alloys such of their mechanical and physical properties as may be of interest as well as their constitution, microstructure and heat treatment. For some time past the bureau has been equipped for the examination and heat treatment of small samples, including the taking of heating and cooling curves in vacuo, in air or other gas. The equipment is being extended to permit the handling of larger test pieces.

Of considerable practical importance in the working of hot metals is the ability to determine their temperatures correctly with optical and radiation pyrometers. Such corrections have been published by the bureau for pure copper and copper-oxide, the experiments for iron-oxide have just been made as well as some preliminary work done on liquid steel, aluminium and oxides. Nickel, special steels and other substances of practical importance are to be studied, the emissivity for each substance throughout the visible spectrum being also determined.

It is hoped shortly to be able to take up some of the high-temperature electro-metallurgical problems, particularly those of interest in furnace design and operation such as electrical and heat conductivity and temperature coefficients of metals, electrodes, furnace materials and charges, carrying the measurements to the actual working temperatures. As to the non-metallic materials of interest to the metallurgist, a paper is in press on the melting points of fire-clays covering representative U. S. samples. A study has also been made of the load-carrying capacity of such bricks at high temperatures, and the determination of the refractory qualities of such material forms a part of the routine work of the bureau.

Another field of usefulness of the bureau is aid furnished in the drawing up of specifications in connection with the technical societies interested and after

experimental study. In the metallurgical field there is room for a great deal of work here. Again, there is the question of nomenclature, for example, of bronzes and brasses, which has been raised before the Institute of Metals, and with new alloys appearing almost every day, some rational system of naming becomes imperative.

In conclusion, it may be said that it is the policy of the Bureau of Standards not to concern itself with those problems that are best treated in private laboratories nor is there any desire to encroach on the field of the consulting engineer or ordinary testing laboratory.

BLOWHOLES IN STEEL INGOTS.*

By J. E. STEAD.

Experiments with a honeycombed ingot of 0.5 per cent carbon crucible steel were made at the works of J. H. Andrew & Co., Ltd., with the assistance of the manager, J. L. Potts, and his melter, Mr. Duckenfield. Two steel ingots from the same mixture were melted in such a way that one was honeycombed and the other sound. The honeycombed steel rose to nearly 10 per cent of its length after teeming, whilst the sound ingot did not rise, but contracted down its central axis.

We may assume that about 9 per cent of the volume of the honeycombed ingot was occupied by blowhole cavities. The ingots were forged to a smaller size after heating to a wash welding temperature, estimated at not less than about $1,100^{\circ}\text{C}$., sufficient to melt the scale on the surface, and were divided into two parts. Half of each set of bars were reheated to $1,100^{\circ}\text{C}$. for one hour, and were then rolled to bars 1 in. in diameter. The remaining halves were heated in the usual way without soaking, and were also forged to 1 in. round bars. All the bars were "reeled" after forging. Portions of each of them were turned down to prisms of $\frac{7}{8}$ in., $\frac{5}{8}$ in., $\frac{3}{4}$ in. and $\frac{1}{2}$ in., and through each a hole was drilled, so as to make a series of cylinders with walls $\frac{3}{16}$ in. in thickness. A similar hole was drilled through portions of the bars which had not been reduced in diameter by turning. The cylinders thus prepared were cut up into a series of rings about $\frac{1}{4}$ in. in depth.

The object of making these rings was to determine the degree to which they could be expanded before breaking, and to see if at their outer polished surfaces they would open out into seams on being slightly strained. The outer parts of the rings were brightly polished, and the rings were expanded by driving into them a hard taper steel drift.

EXPERIMENTS COMPARING SOUND AND HONEYCOMBED INGOTS.

The results need not be given in detail. It is sufficient to state that in no single ring after slight expansion was any unwelded steel detected, and in every case when fracture was effected the steel on each

side of the parting showed evidence of contraction or plastic flow. We may conclude, therefore, that the *surfaces* of the rings were as sound in the steel from the bars of the honeycombed as they were in the steel from the sound ingot, and as there was no difference between the bars with and without soaking, we may be certain that soaking after wash welding, in this case at least, was of no advantage, because the forging in the first instance produced as perfect welding as was possible, and no soaking afterward could improve what was perfection. Although the welding up of the blowholes was apparently good, there was, however, a great difference in the physical properties of the rings from the respective ingots.

The rings from the sound ingot expanded on the average about 50 per cent more before breaking than those from the honeycombed ingot, a peculiarity suggesting at first sight imperfect welding of the blowhole walls. A careful examination of the fractures revealed the presence of dull lines of microscopic fineness in the rings from the honeycombed ingot, while nothing of the kind could be detected in the steel from the sound ingot.

Further, on bending the broken rings from the honeycombed ingot, it was found that some portions of them could be bent to a greater extent without breaking than others, while there was not such variation in the steel from the sound ingot. In the cases where fracture occurred on slight bending these dull lines could almost always be detected on the broken surfaces, but none were present in the portions of the same rings which could be bent to a much greater degree before fracturing. Obviously these dull lines and reduced ability of the steel to extend were correlated.

SEGREGATION OF MANGANESE SULPHIDE.

As the steel contained only 0.02 and 0.03 per cent of sulphur respectively, it seemed improbable with such a small amount of sulphur that there could be any material segregation of manganese sulphide in the blowholes. To determine whether there was or not, cross-sections of the inch bars from the sound and honeycombed steels were cut and polished, and auto-sulphur prints were obtained on bromide paper. The results showed that the sulphur was distributed evenly in the bar from the sound ingot, but was segregated in the places where there had been honeycombs in the unsound ingot. Sulphur prints taken from a cut section of the honeycombed ingot itself also proved that the cavities contained sulphides. We may, I think, be satisfied in concluding that the dull lines are correlated in some way with the sulphide segregation. Finally, sulphur prints of the fractures proved that the dull lines were rich in sulphides.

That clean faces of cavities in crucible steel can be perfectly welded together under treatment identical to that to which the honeycombed ingot was subjected has been fully proved; we are therefore satisfied that the inferior ductility in cross-sections of the bars made

*Extracted by The Iron Age from a paper by J. E. Stead, read before the Iron and Steel Institute, London.

from the honeycombed ingot was due to the presence of sulphide of manganese threads which prevented the metallic faces from completely coming into contact.

BLOWHOLES WITH OXIDIZED WALLS.

During the latter part of the year 1911 a series of trials was made, with the assistance of Mr. Parkin, to determine whether or not artificially formed cavities with oxidized walls could be welded up. It was

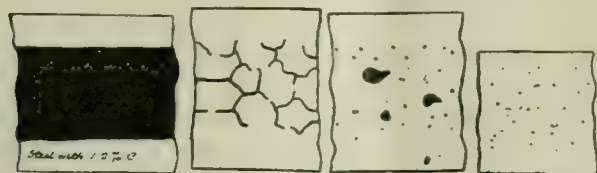


Fig. 1. Fig. 2. Fig. 3. Fig. 4.

taken for granted that if no carbon were present in the steel, oxidized blowholes could not be perfectly welded. In the first experiment with a 2-in. square steel bar about 8 in. in length containing 1.2 per cent carbon, a small hole was drilled nearly to the bottom, along the central axis. The bar was then heated to redness and oxygen gas was blown down the hole, so as to oxidize the walls of the cavity. After heating to about 900° C. it was hammered, so as to bring the sides of the cavity into juxtaposition. The bar was then heated to and maintained at a temperature of about 1,100° C. for one hour, and was at once forged down to a smaller size. When cold it was nicked at intervals and broken at the nicks, and the fractures examined. They indicate imperfect welding near to what was originally the open end of the bar, but below this for two-thirds of the length the welding appeared to be perfect.

On microscopic examination of the polished cross-sections of the parts where welding appeared to be good it was found that the seam, originally consisting of oxide of iron, had been practically reduced to the metallic state, with the exception of minute globular dust-like inclusions, probably of iron or manganese silicate—the residue of the oxidized steel which was incapable of being reduced by the carbon. But for these excessively minute inclusions the welding was perfect. On bending a polished and etched section to open the joint, the metal at this point being lower in carbon than the surrounding mass, extended and then broke, showing a perfectly crystalline fracture, a proof that good welding had been effected.

EFFECT OF SOAKING AND FORGING.

In a second experiment with the same steel a bar was prepared as above described, with the exception that after the cavity was oxidized and closed the bar was heated to 950° C. for three hours. It was then cut in half; one-half was retained for examination, the other was reheated at 1,100° C. for one hour, and without forging, it was allowed to cool. It was again cut into two portions, one of which was heated to 1,100° C. and then forged down to a smaller size. The

other part was reserved for examination. Each of the three specimens was sectioned, polished and examined microscopically without etching.

Figs. 1 and 2, representing magnifications of 330 diameters, show that by heating at 950° C. the carbon of the steel reduced the iron scale to metallic iron, which remained in separate grains, surrounded either by some slight amount of unreduced oxide, or gaseous spaces, or by both.

On attempting to bend the specimens, the grains at once separated; there was no cohesion, they had not completely crystallized together—a result not surprising, for the volume of metallic iron is less than that of its oxide.

Fig. 3 represents the same bar as the last after heating to 1,100° C. for one hour. The drawing shows that the greater mass of the reduced iron grains had crystallized together and pressed to one side the intervening gases, and compelled them to segregate into relatively large bubbles at a considerable distance from each other. The micro-structure of the joint in the

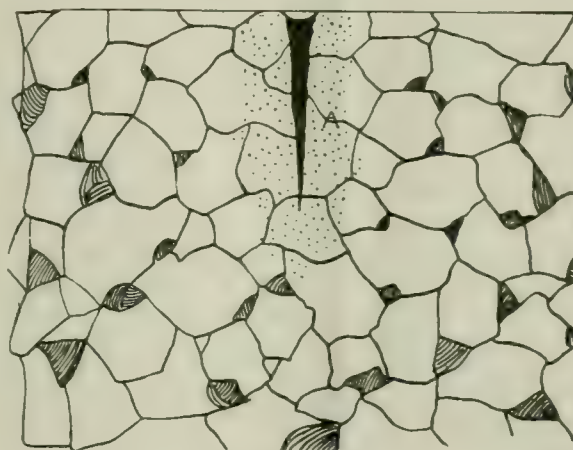


Fig. 5.

third portion, which had been reheated to and forged from 1,100° C., was identical with that in the bar of the first experiment, which had been heated to 1,100° C. for one hour and then forged to a smaller size, and is represented in Fig. 4. The welding was perfect, with the exception of the minute globular inclusions previously referred to.

In a third experiment the steel bar was treated exactly as in the first, but the bar itself contained only 0.50 per cent carbon. The welding was found to be complete, but the joint previously occupied by the scale now consisted of carbonless ferrite, and the adjacent steel contained less carbon than the mass of the steel itself. These results show, as was anticipated, that if the walls of the cavities are not too thickly scaled and a sufficient quantity of carbon is in the steel, the scale itself can be reduced practically entirely to the metallic state, and this can be welded up to the sides of what was originally the cavity.

SIGNS OF BLOWHOLES IN AN AXLE.

It is generally assumed that blowholes, which terminate on one side through the outer skin of the en-

velope of steel ingots, having access to oxidizing gases, get so severely oxidized on their walls that no welding of the cell walls occurs, and that in rolling out they are simply extended and appear at the surface of the rolled sections as rokes, which penetrate to the full depth of the extended blowholes.

It is only necessary to describe a single instance. This was a railway axle, on the surface of which there was ample evidence of pre-existing cutaneous blowholes in the ingot, for at intervals there were longitudinal lines or fine grooves an inch or more in length. A cross-section vertical to the surface, after polishing, was sufficient to reveal the position and depth of these rokes. The depth varied from one-hundredth to one-fifth of an inch. The outer envelope was completely decarburized, as is usual in low and medium carbon steels which have been reheated in an oxidizing atmosphere previous to forging or rolling.

There was a complete absence of the minute inclusions in this envelope; the steel contained no carbon, but the ferrite immediately in contact with the scale, and for a little distance beyond, contained minute globular inclusions, while at a greater distance the crystals of iron contained none.

The diagrammatic sketch, Fig. 5, explains better than words the appearance under the microscope. There can be little doubt that the ferrite containing the inclusions surrounding the remaining unreduced oxide was at one time oxide or scale in a blowhole, that this was reduced practically entirely to the metallic state by the carbon in the adjacent steel, and that the particles of reduced iron had crystallized together and to the steel itself, producing a practically perfect weld—indeed, on straining, so as to bend the steel, there was no opening out at the junction of the two zones. The minute inclusions are the residual portion of the scale which could not be reduced by carbon or carbon monoxide at the temperature at which the steel had been heated and rolled.

CONCLUSION.

In conclusion, it seems reasonable to believe that under the ordinary treatment to which honeycombed ingots of steel are heated and rolled, internal small cavities or blowholes do become perfectly welded up, provided there is an absence of sulphide segregations, and that even when these segregations are present, as they are not in continuous lines but occur only at intervals, the clean metallic faces between them come into contact and weld together.

It seems also justifiable to conclude that surface blowholes, which become oxidized on their walls during the heating and rolling of the ingot, do become more or less completely welded. The conditions favorable to this welding must be sufficiently high temperature, and maintenance of the steel at that temperature for a long enough period after the cavities have been closed, to admit of the carbon in the adjacent steel being afforded the opportunity to reduce the oxide scale.

ON THE SIMULTANEOUS ELECTROLYTIC DEPOSITION OF COPPER AND ZINC FROM VARIOUS SOLUTIONS NOT CONTAINING CYANIDE.*

By M. DE KAY THOMPSON.

The use of potassium baths for electroplating with gold, silver, zinc and other metals was discovered simultaneously and independently by Elkington and Ruolz in 1841.¹ Brass plating was first carried out by means of a cyanide bath by Ruolz in 1842,² though cyanide baths were not introduced into practice at first on account of their high cost.³ At present brass plating is done only from a bath of potassium zinc and potassium copper cyanide, with a small excess of potassium cyanide. The cyanide brass bath is not entirely satisfactory, as it is slow and discoloration in spots is likely to appear after the surface has been polished and lacquered.⁴

Of the numerous different brass plating baths or brass plating methods that have been published or patented since the discovery by Ruolz of the use of cyanides for this purpose, there seem to have been only two in which cyanides were absent. The first was invented by Brunel Bisson and Gauguin⁵ in 1848 and has the following composition: 500 parts of potassium carbonate, 20 parts of copper chloride, 250 parts of ammonium nitrate and 40 parts of zinc sulphate. The volume in which these salts are dissolved is not given. In order to test this bath the above figures were divided by ten and these numbers of grams were dissolved (except for a small residue) in 450 cubic centimeters of water and electrolyzed with brass anodes and a platinum cathode. The temperature was 25° C. and the current density in the different experiments varied from 0.55 to 2 amperes per square decimeter. This bath proved to be of no value, for the deposits were in all cases copper, as was evident from their appearance.

The second method of brass plating without cyanides, referred to above, consists in using a sulphate solution of copper and zinc with rotating cathode and anodes of copper and zinc on opposite sides of the cathode.⁵ A high electromotive force from one dynamo was applied between the zinc and cathode and a low electromotive force from another dynamo between the copper and the cathode. The return wire from the cathode was common to both dynamos. By this arrangement it is said brass could be deposited on the cathode. It is rather difficult to see how brass could be obtained in this way, however, for in sulphate solutions of equal ionic concentration the potentials of zinc and copper are over a volt apart, and this cannot be very much reduced by making the zinc concentrated and the copper dilute. If the current density is increased greatly with the idea of reaching the

*From Metallurgical and Chemical Engineering.

¹Comptes Rendus 13, 998-1021 (1841). The dates of the patents are Elkington, 8 Dec., 1840; Ruolz, 19 Dec., 1840.

²Comptes Rendus 15, 446 (1842).

³Chem. Centralbl., 1848, 506-508.

⁴Hogaboom, Trans. Am. Electrcch. Soc. 19, 53-56 (1911).

potential difference between solution and cathode at which zinc would be deposited copper is certain to come down in a spongy form. Whether the current starts from a copper or a zinc anode only affects the composition of the bath and has nothing to do with determining which metal is deposited on the cathode at any given instant. A similar method to that of Jacobs was patented in 1858 by S. J. Goode for controlling the composition of cyanide baths,⁶ though separate dynamos were not used. The current through the anodes was regulated by changing the depth to which they were immersed or their distance from the cathode.

It was thought that it would be an interesting subject for investigation to see whether some other than the usual cyanide bath could not be found from which brass could be plated and which would not have the disadvantages of the cyanide bath. This is the subject of the following paper.

In order to get a good electrolytic deposit of a metal the bath must not be too dilute with respect to the metal, but in order to have two metals whose electrolytic solution pressures are widely different deposit simultaneously, it is necessary that the ionic concentration of the less electropositive metal should be reduced to such a degree that the two potentials of the two metals in the solution should be nearly equal, that is:

$$\frac{RT}{n_1 F} \log \frac{P_1}{p_1} = \frac{RT}{n_2 F} \log \frac{P_2}{p_2}$$

Where the subscripts refer to the two metals and the letters have the usual significance. It is not necessary that exact equality should exist, for the potentials at which the two metals deposit are reduced if they form an alloy at the instant of deposition, and also the concentration change taking place near the anode increase the potential difference between the cathode and the solution when the current is passing.⁷ The only way in which low ionic concentration can be obtained with a comparatively large amount of the metal in solution is to have the metal in the form of a complex salt. If the ionic concentrations of both metals were equally reduced in any given complex not much relative change would be produced in the potentials of the two metals. Copper, however, has a much greater tendency to form complexes than zinc, and its potential is changed much more than that of zinc in the case of the cyanide solution⁷ and probably in other cases also.

In attempting to find a bath from which copper and zinc can be deposited simultaneously the obvious thing to do was to try all the possible complex salts of copper. In order to measure out easily any desired amount of copper or zinc sulphate for making the complex salt solutions, a solution of copper sulphate containing one gram atom of copper per liter and another containing two gram atoms of zinc per liter

were made up. The cathode used in the following experiments was polished platinum. The following is an account of the experiments with various complex salts:

1. The additions of glycerine, of sugar and of tartaric acid to the solution of a copper salt prevent some of the ionic reactions of copper, which indicates the formation of complex salts.⁸ A bath was made up containing 0.25 gram atom of copper, 0.25 gram atom of zinc and 250 cubic centimeters of glycerine per liter. This was electrolyzed at room temperature with 2.6 and 1.6 ampere per square decimeter. The appearance of all of the deposits obtained showed them to be copper.

2. Sugar.—The effect of cane sugar was tested by electrolyzing a solution containing 0.5 gram atom of copper, 0.5 gram atom of zinc and 50 grams of sugar per liter. The current density was 3.3 amperes per square decimeter. This being very high, precipitated copper in a spongy state, but there was no evidence of zinc, as shown by the color.

3. Tartaric Acid.—A solution containing 0.5 gram atom of copper, 0.5 gram atom of zinc and 0.5 formula weight of tartaric acid was electrolyzed with 0.33 ampere per square decimeter. Only copper was deposited.

4. Glycocoll.—The addition of glycocoll to the solution of a copper salt produces a deep blue color and a very complex salt of the formula $\text{Cu}(\text{NH}_2\text{CH}_2\text{COO})\text{H}_2\text{O}$, which is only partially precipitated by hydrogen sulphide. This seemed therefore to be promising, but on electrolyzing a solution containing 0.5 gram atom of copper, 0.5 gram atom of zinc and 100 grams of glycocoll per liter only copper was obtained. The current density was 3.85 amperes per square decimeter. At 60° C. the deposit was also copper, but of a lighter color. In cyanide baths the more free potassium cyanide is present the more the ionic concentrations of copper and zinc are reduced. It was not found, however, that 50 per cent more glycocoll added to the above bath had the effect of causing zinc to be deposited with the copper. This result is probably due to the formation of a very complex zinc salt, as explained above.

5. Sodium Potassium Tartarate.—A solution of copper was made according to Brown and Mathers⁹ containing in 1,000 grams of water 60 grams of copper sulphate (0.24 gram atom of copper), 50 grams of sodium hydrate and 159 grams of sodium potassium tartrate. On dipping metallic zinc into this solution it slowly becomes colored with a dark iridescent layer. A zinc solution was made from zinc sulphate and sodium hydrate containing 10.24 gram atom of zinc and 140 grams of sodium hydrate in 1,000 grams of water. Equal volumes of these solutions were mixed and the resulting bath electrolyzed with a current density of 0.3 ampere per square decimeter. The deposit was smooth, adhered well and had a rich

⁵Charles B. Jacobs, Jour. Am. Chem. Soc. 27, 972-76 (1905).

⁶Chem. Centralbl., 1858, p. 350.

⁷Spitzer, Zeit. f. Elektroch. 11, 345-68 (1905).

⁸Abegg, Handbuch der anorg. Chem. 2, 547 (1908).

bronze color. The deposit was analyzed qualitatively and was found to contain some zinc. The same solution was electrolyzed with 0.6 ampere per square decimeter. The deposit was of a paler color and also contained zinc.

A bath was made from 150 cubic centimeters of the zincate solution and 50 cubic centimeters of the copper tartrate solution. On electrolyzing this with a current density of 0.3 ampere per square decimeter the deposit was similar to that obtained with the same current density in the solution made from equal volumes of the zinc and copper solutions, except that it was streaked in places with a granular deposit. This deposit also contained zinc. A great reduction in the total amount of copper in solution does not improve the deposit in this case nor in any other studied in this connection. Very little hydrogen was liberated on electrolyzing these solutions.

6. Thiosulphate.—On adding a solution of sodium thiosulphate to a copper salt the color changes to bright green and then to yellow, finally becoming colorless, with a large excess of the thiosulphate.¹⁰ On electrolyzing a solution containing 0.4 gram atom of copper, 0.4 gram atom of zinc and 280 grams of sodium thiosulphate per liter, with a current density on the platinum cathode of 1.94 amperes per square decimeter, with brass anodes, a flaky bronze colored deposit was formed which did not adhere well to the cathode. This deposit was washed well with water and dissolved in nitric acid, except a small residue, which seemed to be sulphur. The amount of copper contained was determined electrolytically. The zinc was determined by precipitating with diammonium hydrogen phosphate as described in Talbot's "Quantitative Analysis." The results of a single analysis were the following:

Copper	50.5 per cent
Zinc	41.0 per cent
Deficit	8.5 per cent
	100.0

The deficit of 8.5 per cent is probably due to the residue which did not dissolve in nitric acid. The residue is probably also the cause of the bronze color. On allowing this solution to stand over night a muddy precipitate formed. It would therefore not be of any practical importance even though a good deposit could be obtained from it.

7. Phosphorous Acid.—The addition of phosphorous acid to a copper salt produces a complex copper phosphite anion.¹¹ A solution containing per liter 0.5 gram atom of copper, 0.5 gram atom of zinc and 50 cubic centimeters of phosphorous acid of 1.2 specific gravity was electrolyzed with a cathode current density of 1.33 amperes per square decimeter. A deposit of copper was obtained. On adding 10 cubic centimeters more of the acid to 100 cubic centimeters of this bath the deposit was the same.

8. Ammonia.—The deep blue color produced by

adding ammonia to the solution of a copper salt is due to a complex copper ion, and it has been stated that the ammoniacal solution of copper and zinc is one of a number of others from which zinc and copper can be deposited simultaneously.¹² It was found that only copper is deposited from a solution containing 0.225 gram atom of copper, 0.225 gram atom of zinc and 660 cubic centimeters of strong ammonia per liter. This amount of ammonia precipitated and then dissolved the two metals.

9. Thioglycollate.—Salts of thioglycollic acid, $\text{CH}_2\text{-SHCOOH}$, form complex salts with copper when added to a copper salt solution.³ The potassium salt of thioglycollic acid was prepared by the method of Claesson,¹⁴ which consists in adding one mol of monochloroacetic acid to a solution of two mols of potassium sulphhydrate. The potassium chloride was filtered off and the filtrate treated with several times its volume of strong alcohol, which dissolves most of the potassium thioglycollate. After boiling off the alcohol the residue of white potassium thioglycollate was dissolved in water and added to 5 cubic centimeters of the copper solution, producing a bluish black precipitate which slowly turned white. This is the salt $(\text{HOCOCH}_2\text{S})_2\text{Cu}_2$. This was filtered and dissolved in strong hydrochloric acid. The final solution contained 0.046 gram atom of copper, 0.36 gram atom of zinc, and was clear and colorless. The zinc sulphate was added to the copper glycollate without producing a precipitate. Electrolyzed with 0.07 ampere per square decimeter, only copper was deposited. On electrolyzing with a higher current density the solution became muddy.

10. Oxalate.—Copper oxalate forms a complex when dissolved in an excess of ammonium oxalate, in which the copper is in the anion.¹⁵ A bath was made up containing in one liter 5 grams of oxalic acid, 55 grams of ammonium oxalate, and 15 grams of copper sulphate, as a similar solution, slightly more dilute, was found a good starting point for bronze plating.¹⁶ When a zinc rod was dipped into this solution it took several minutes for it to become covered with a layer of copper, and when finally covered the copper was bright and adhered firmly. A solution of zinc was made from 12 cubic centimeters of the stock zinc sulphate solution and 40 grams of ammonium oxalate in one liter, corresponding to 0.024 gram atom of zinc per liter. A bath was made by mixing 150 cubic centimeters of the zinc solution with 50 cubic centimeters of the copper, corresponding to 0.015 gram atom of copper, 0.021 gram atom of zinc, 1.25 gram of oxalic acid, and 43.8 grams of ammonium oxalate per liter. With 0.17 ampere per square decimeter the deposit was spongy and apparently only copper. With 0.51 ampere per square decimeter the deposit was spongy and dark. It was washed and analyzed qualitatively

¹²J. L. R. Morgan, Jour. Am. Ch. Soc. 22, 93-99 (1900).

¹³Abegg, l. c., p. 559.

¹⁴Liebig's Ann. 187, 113-126 (1877).

¹⁵Abegg, l. c., p. 549.

¹⁶Curry, Jour. Phys. Chem. 10, 515-20 (1906).

¹⁰Abegg, l. c., p. 557.

¹¹Abegg, l. c., p. 546.

for zinc; none was found present. With 1 ampere per square decimeter the deposit looked like brass in places and was found to contain zinc.

A solution was then made by mixing 25 cubic centimeters of the zinc oxalate solution and was electrolyzed with a cathode current density of 0.33 ampere per square decimeter. This gave a dark deposit. With 0.15 ampere per square decimeter the deposit was dark and easily wiped off.

Another solution made by mixing equal portions of the copper oxalate and the zinc oxalate solutions, thus containing in one liter 0.03 gram atom of copper, 0.024 gram atom of zinc, 2.5 grams of oxalic acid and 47 grams of ammonium oxalate. On electrolyzing with 0.28 ampere per square decimeter a deposit was obtained which first looked like smooth copper, but which later became granular. On increasing the current to 0.56 ampere per square decimeter, the deposit had a light brown color, and was found to contain zinc. The deposit had a similar appearance with a current density of 0.84. Hydrogen was liberated in all the electrolyses in oxalate solutions.

With this solution a rather curious observation was made. On repeating the electrolysis in the last mentioned bath with a current density of 0.56, the light brown deposit was not obtained, but the deposit seemed to be granular copper. On changing the platinum cathode for another, the light deposit was again produced. It is therefore evident that the cathode itself is of some consequence in determining the nature of the deposit. This experiment was repeated several times with the same result.

II. Pyrophosphate.—The nearest approach to success was with the solution made by dissolving zinc and copper pyrophosphate in an excess of sodium pyrophosphate.¹⁷ Good deposits of zinc or of copper could be obtained from solutions containing only zinc or copper pyrophosphate. A solution was then made containing 0.054 gram atom of zinc, 0.054 gram atom of copper, and 108 grams of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ per liter. This sodium pyrophosphate includes that used to precipitate the metals and to redissolve them. On electrolyzing this solution with brass anodes and a platinum cathode with a cathode current density of 0.83 ampere per square decimeter a brassy looking deposit was obtained. It was tested qualitatively for zinc, which was found present. There is a large polarization at the anode apparently caused by the resistance of a salt produced by the action of the current on the anodes, which does not dissolve readily at room temperature. If the solution is heated to 60 deg. C. this salt does not appear on the anodes. The deposit on the cathode is also good when obtained from a hot solution, but both in the hot and the cold solutions the deposit remains smooth and of a brassy appearance only for a short while. When the electrolysis is prolonged, the deposit becomes discolored, or granular. The solution around the cathode also becomes quite

alkaline, as was noticed by the slippery feeling of the cathode on removal from the solution. If the cathode is rotated in order to stir up the solution in its neighborhood only copper is deposited by the current, which shows that the action of the current is partly responsible for producing the proper concentrations of copper and zinc ions near the cathode for depositing both metals together. It seemed that the alkalinity of the solution around the cathode caused the copper to form an oxide, thus spoiling the deposit. Various proportions of copper and zinc were tried without observing any improvement. The deposit is very much changed by a small change in the current density. The cathode frequently had an entirely different appearance in the center and on the edges, doubtless due to a slightly different current density at these points. In no case did the deposit continue to have a smooth surface when the electrolysis was prolonged. If the current density was low, only copper came down.

If a zinc rod is dipped into a solution of copper pyrophosphate, copper is deposited only very slowly, adhering firmly.

A deposit was obtained with a rotating platinum cathode frequently of a very light color like zinc, but on touching with a drop of nitric acid it turned copper colored immediately. It would seem therefore that this color is due to some oxide or hydrate of copper.

As the alkalinity of the solution around the cathode seemed to be the cause of the change in the appearance of the deposit, an attempt was also made to prevent the solution becoming alkaline by holding the pyrophosphate of zinc and copper in solution with pyrophosphoric acid. Free pyrophosphoric acid hydrolyzes slowly, changing to phosphoric acid, but there was a possibility that it would not do so when combined with these salts.

Pure copper pyrophosphate was made by adding an excess of copper solution to a hot solution containing 11.2 grams of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, which forms 0.025 of a formula weight of copper pyrophosphate. This was washed with decantation with hot water until the wash water gave no test for sulphates. It was then filtered and transferred to an Erlenmeyer flask while moist. Then a fresh standardized solution of pyrophosphoric acid was run in from a burette until the solution became clear. A solution of zinc pyrophosphate in pyrophosphoric acid was prepared in the same way. The commercial pyrophosphoric acid was standardized against a solution of sodium carbonate with methyl orange as an indicator, taking into account that when the end point is reached only two hydrogen ions have been neutralized.¹⁸ It was found that one formula weight of pyrophosphoric acid would dissolve 0.5 of a formula weight of zinc pyrophosphate, the final volume being 3.7 liters for the above amounts of acid and salt. In the case of copper 1.35 formula weight of the acid was required for 0.5 formula weight of copper pyrophos-

¹⁷ Abegg, *l. c.*, p. 546.

¹⁸ *Jour. Am. Ch. Soc.* 30, 735 (1908).

phate. The final volume here was 2.96 liters. With a rather high current density zinc could be deposited from the zinc pyrophosphate solution with the simultaneous evolution of hydrogen. Copper was easily deposited from its solution without evolving hydrogen. A solution containing both copper and zinc pyrophosphates was made by mixing these solutions, so that there was 0.15 gram atom of zinc and 0.15 gram atom of copper per liter. On electrolyzing this with brass anodes and varying current densities, the highest being 1 amp per square decimeter, only copper and hydrogen were deposited. The acid solution is therefore not as complex as when the salts are held in solution by sodium pyrophosphate.

On standing over night some of the zinc and copper pyrophosphate precipitates, showing that the combination with these salts does not prevent the hydrolysis of pyrophosphoric acid.

SUMMARY OF CONCLUSIONS.

Eleven complex copper salts were made by the following agents and were electrolyzed after mixing with zinc sulphate solution; glycerine, cane sugar, tartaric acid, glycol, sodium potassium tartrate and sodium hydrate, thiosulphate, phosphorous acid, ammonia, thioglycollate, oxalate and sodium pyrophosphate. The only solution which gave a smooth, bright deposit when electrolyzed for an hour or more was the alkaline sodium potassium tartrate solution. This deposit, however had a bronze color.

The solutions from which appreciable amounts of zinc were deposited with copper were the alkaline potassium sodium tartrate, the oxalate and the pyrophosphate.

It was not found in any case that diminishing the total amount of copper in the solution improved the deposits. It seems that the complexity of the copper salt must be relied on to reduce the concentration of the ions sufficiently, while there must be enough copper present in the unionized state to furnish ions as rapidly as they are used up.

A select committee of the House of Commons on patent medicines has been holding sessions for some time past in London. The purpose of the committee is to make a thorough investigation in reference to the law with regard to the sale and advertisement of patent medicines in the United Kingdom, and to make suggestions and recommendations—if they deem it advisable to do so—with regard to changes that should be made. In the course of the inquiry it was shown that three years ago even no fewer than 41,757,535 patent-medicine stamps were sold in the United Kingdom. This was practically equivalent to one package of patent medicine for every man, woman and child in the country. The gross receipts from the sale of the stamps was £355,000 (\$1,727,608). The receipts for the year ending March 25, 1912, was £327,856 (\$1,595,510).

FUEL BRIQUETS IN AMERICA.

Some progress has been made in the development of fuel briquetting in the United States during the last two years, but this country still lags far behind some European countries, notably Germany. In 1911 the American production was 218,443 tons, valued at \$808,721—almost double that of 1909. The subject of briquetting is one to which attention should be given, as on it depends to a considerable degree the utilization of some grades of fuel which should be made useful but which are now wasted or sold at less than the actual cost of production. The reprehensible but apparently growing practice of shooting bituminous coal "off the solid" (and this is notably prevalent in the non-coking coal fields of the Mississippi Valley) produces an inordinate proportion of slack, an undesirable product which it is difficult or impossible to sell, and, in fact, by the best mining practice the quantity of slack produced is frequently too large to be profitably disposed of. Some of it, quite significant quantities indeed, are used as powdered fuel in the manufacture of cement; but its use under boilers is unsatisfactory, as in the high heat of combustion the ash is fused and is deposited as a glassy material on the boiler tubes, and thus eventually produces an insulating covering which destroys the efficiency of the plant. The principal factor militating against the more rapid development of fuel briquetting in the non-coking coal fields of the Middle West is the low price of the raw fuel with which the manufactured product has to compete, and as long as new areas can be opened without restriction and the supply of cheap coal continued, so long will the present profligacy be maintained and the slack continue to be unused except to a limited degree.

The U. S. Consul at Para, Brazil, reports under date of July 15 that final arrangements have been concluded between the Bank of Brazil and the parties interested in and forming the syndicate organized in 1910 to increase the price of rubber, whereby the latter will, under conditions as yet unknown, take charge of and dispose of the same. The amount of rubber held by the Bank of Brazil as collateral for money advanced to finance the aforementioned scheme is 2,400 tons. The Consul states that he is informed that it is the present intention of the directors in charge of this liquidation to dispose of this rubber to bona fide manufacturers only, hoping in this way to avoid manipulation by dealers who might be interested in affecting the price of the coming crop. He is further informed that the rubber is only to be sold and shipped from here, as its storage in either London, Liverpool, or New York might have the effect of depressing present prices. This rubber is all of first quality, being bone-dry, and should on its merits command a higher price than new rubber.

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HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

The Expert Witness.

The engineering profession in general have sometimes met with severe criticism on account of the conduct of some of the members when appearing in court as experts.

The chemical engineer has not been fortunate enough to escape this general criticism. We have our chemical engineers whose principal occupation seems to be that of "expert" in various matters under litigation. It does not matter much what the case may be or the bearing of the technical question upon which he is supposed to supply an expert opinion; it may be a question of the chemical treatment of a South African gold ore or the historic question of "What is whiskey?" he is just as ready to qualify as an expert on one as on the other, and his opinion will depend very much upon the party to the litigation who first becomes impressed with the qualifications of our expert and engages his services.

We are thankful that such experts form an insignificant minority in our profession and that the well-known men in the profession are far above such practices. A little such work, however, goes far towards discrediting the opinion of the well qualified,

conscientious men who are truly experts in their lines of work and who do not seek to pose as such in other lines.

These true experts are usually so occupied in the studies upon which their reputations are based, and having as well a distaste for this kind of publicity, their merits are not placed before the parties in litigation, but you may be sure no such condition arises in the case of our professional expert.

The condition many times arises when it is difficult to select a man who is expert on the subject in question. It may take a man who is quite conversant with the general subject to point out the one who is pre-eminent in that line; the parties to litigation more often than not lack this general knowledge requisite for a judicious selection of an expert, and in many instances do not know where to go for impartial advice.

Several European countries have established separate technical courts for the trial of technical cases and supplied these courts with a corps of technical advisers, who are always at the service of the court; the court is also permitted to employ other persons as experts when it is deemed advisable to do so.

The establishment of such judicial procedure in this country would be a great step in the elimination of the evils of the expert witness. It would give us a court with some technical knowledge and would enable this court to ascertain the facts on the question in litigation from men who, being paid by the court, have no pecuniary interest in the outcome of the case.

This question of the expert witness, together with that of the separate technical court, will be ably discussed before the section on law and legislation at the Eighth International Congress of Applied Chemistry. Papers are promised by some of our European friends thoroughly conversant with their procedure and what it has accomplished, as well as papers from leaders in science and jurisprudence in this country. The suggestions embodied in these papers will be received with great interest.

THE EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

The congress will open its sessions in Washington on Sept. 4. The sessions in Washington will be chiefly of a formal nature. The presentation of papers will commence in New York City on Sept. 6.

A number of papers are promised from noted European chemists and practically all of our own best known men will be represented on the program in some section.

This will undoubtedly be the greatest gathering of chemists and chemical engineers which has taken place in this country.

Nearly 700 papers have been promised for the various sections.

We publish below the titles of some of the papers which seem most likely to be of interest to the chemical engineer:

GENERAL PAPERS.

Dr. F. Raschig: The Scientific and Technical Importance of Tar-phenols.

Dr. F. W. Frerichs: Thirty-two Years in the United States as Chemist and Manufacturer.

Public lecture by Gabriel Bertrand of Paris, France, entitled *Du rôle des infiniment petits chimiques en chimie biologique*, Great Hall, College of the City of New York.

Samuel Eyde of Kristiana, Norway, entitled *Oxidation of Atmospheric Nitrogen and Development of Resulting Industries in Norway*.

Public lecture by Carl Duisberg of Elberfeld, Germany, entitled *Die Neuesten Arbeiten und Probleme der Chemischen Industrie* (the lecture will be delivered in English), Great Hall, College of the City of New York.

General lecture by William Henry Perkin of Manchester, England, entitled *The Permanent Fireproofing of Cotton Goods*, Great Hall, College of the City of New York.

Joint meeting of the sections on inorganic chemistry, physical chemistry, electrochemistry and agricultural chemistry at the College of the City of New York. Address by H. A. Bernthsen of Ludwigshafen-on-Rhine, Germany, entitled *Synthetic Ammonia*.

SECTIONAL PAPERS.

J. M. Camp, chief of bureau of instruction, Carnegie Steel Company, Munhall, Pa., *The Methods of the United States Steel Corporation for the Commercial Sampling and Analysis of Pig Iron*.

Pontus H. Conradson, Galena Signal Oil Company, Franklin, Pa., (1) *Apparatus for Evaporation of Cylinder and Valve Oils in Steam, Air and Other Gases*. (2) *Method and Apparatus for the Determination of Sulphur in Petroleum Oils*.

L. F. Hawley and R. C. Palmer, forest products laboratory, Madison, Wis., *The Relative Yields Obtained by the Destructive Distillation of Different Forms and Species of Hardwood*.

Dr. C. S. Hudson, bureau of chemistry, United States department of agriculture, Washington, D. C., *Studies on the Hydrolysis of Sucrose and Raffinose by Invertase*.

William Raitt, Forest Research Institute, Dehra Dun, India, *Bamboo Cellulose*.

G. B. Shipley, president Pittsburgh Wood Preserving Co., Pittsburgh, Pa., *Detailed Design and Construction of Modern Wood Preserving Plants*.

C. C. Tutweiler, chemist, United Gas Improvement Co., 1706 N. Broad St., Philadelphia, Pa., *The Fractionation and Analysis of Creosote Oils*.

Chas. M. Bullard, 93 Broad St., Boston, Mass., *Scientific Control in Sulphite Pulp Manufacture*.

H. F. Bauer, 308 Madison Ave., Waukegan, Ill.,

Notes on the Preparation of Chemically Pure Dextrose.

Hans Wrede, 74 Hudson St., Hoboken, N. J., *Combination of Starch and Minerals for Paper Sizings*.

C. A. Crampton, 617 Evans Bldg., Washington, D. C., *The Use of Tax-Free (denatured) Alcohol in the United States*.

Theodore Sedlmayr, Ph. D., 51 Traders' Bldg., Chicago, Ill., *The Scientific Control of Malting Operations*.

Robert Wahl, Ph. D., the Wahl-Henius Institute of Fermentology, 1135 Fullerton Ave., Chicago, Ill., *The Enzymes of Malt*.

Francis Wyatt, the National Brewers' Academy, 402 W. 23rd St., New York City., *Some Inconsistencies in the United States Standards for Malt Vinegar*.

Virgil Coblentz, Ph. D., Brooklyn, N. Y., *Estimation of Citric Acid in Commercial Calcium Citrate*.

Dr. James Aston, Madison, Wis., *Corrosion Tests of a Series of Iron Alloys*.

Dr. F. A. J. Fitzgerald, Niagara Falls, N. Y., *Heat Losses in Furnaces*.

Dr. W. H. Walker and Mr. Walter A. Patrick, Massachusetts Institute of Technology, Boston, Mass., *Determination of Total Oxygen in Iron and Steel by Means of Carbide Formation*.

Dr. Warren K. Lewis, Massachusetts Institute of Technology, Boston, Mass., *Electrolytic Oxidation of Sugar and Oxalic Acid*.

Dr. Wm. H. Walker and Ralph E. Gegenheimer, Massachusetts Institute of Technology, Boston, Mass., *Factors Controlling the Cost of Sodium-Hypochlorite Production*.

W. C. Ferguson, Laurel Hill, N. Y., *Organized Research and Analytical Chemistry: Their Function for Successful Chemical Manufacturers*.

S. W. Parr, M. S., University of Illinois, Urbana, Ill., *a New Alloy With Acid Resisting Properties*.

Chas. A. Doremus, 55 W. 53rd St., New York City, *Commercial Production of Pure Alumina from Kaolin*.

H. R. Moody of the College of the City of New York, *Nitrogen Fixation*.

Prof. Edw. Hart, Ph. D., Lafayette College, Easton, Pa., *The Extraction of Potash from Feldspar*.

F. T. Snyder, Monadnock Bldg., Chicago, Ill., *The Electric Smelting of Zinc Ore*.

Robt. Adan, 33 rue de Flandre, Gant, Belgium, *Micrographie des Fontes Speciales de Fer*.

J. A. Matthews, Halcomb Steel Co., Syracuse, N. Y., *Some Physical Characteristics of High Speed Tool Steel*.

Dr. Rudolf Ditmar, Handels-Laboratorium, Graz 111, Vinzenzorgasse 24, *Die Chemische Analyse von Gutta-Persha*.

Dr. F. Willy Hinrichsen, Landhaus Weiss, Machnower Chaussee, Berlin-Zehlendorf, Amt Zehlfd (1147), *Technology of Rubber*.

Dr. F. E. Junge, Gortitz, Germany, *Recent Progress in the Rational Utilization of Coals in Germany*.

A. C. Langmuir, Valuation of Crude Glycerine for Refining Purposes.

D. P. C. McIlhiney, 7 E. 42nd St., New York City, The Analysis of Varnish.

O. Eisenschiml, 110th St. and Torrence Ave., South Chicago, Ill., A Critical Review of the Laws and Specifications of Linseed Oil.

Dr. Albert Sommer, Barber Asphalt Paving Co., Land Title Bldg., Philadelphia, Pa., Petroleum Turpentine Substitutes.

H. E. Surface, Forest Products Laboratory, Madison, Wis., The Effect of Variable Cooking Conditions on the Production of Soda Pulp.

H. C. Humphrey, Corn Products Refining Co., 17 Battery Place, New York, The Influence of the Utilization of By-products on the Development of the Industry of Corn Products.

Dr. C. B. Thwing, 445 N. Fifth St., Philadelphia, Pa., A Controlling Device for Electric Furnaces.

Prof. Otto L. Kowalke, University of Wisconsin, Madison, Wis., Observations on the Base Metal Thermo-couples.

Dr. E. G. Fink, General Electric Co., Harrison, N. J., New Applications of Ductile Tungsten and Molybdenum.

Dr. P. Heroult, 73rd St. and Broadway, New York, Recent Developments in the Electric Steel Furnace.

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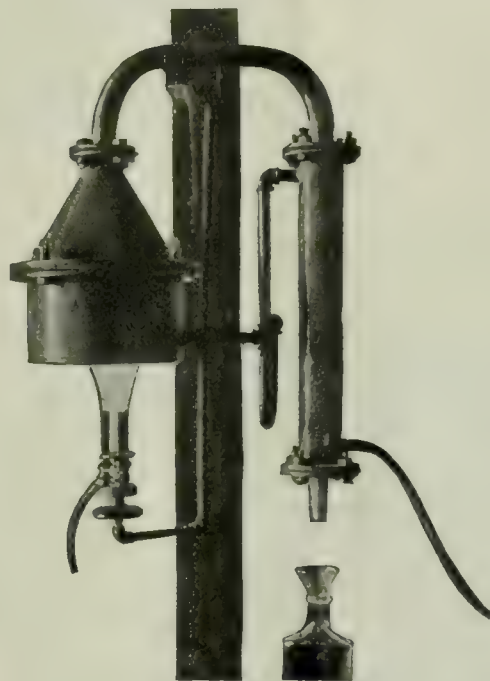
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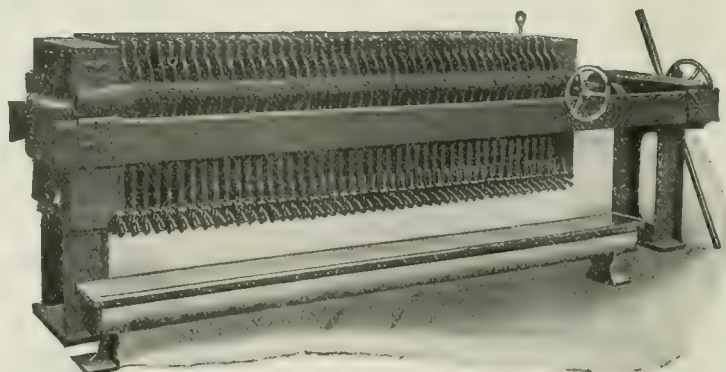
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Meade's "Design and Equipment of Small Chemical Laboratories" is, from cover to cover, excellent in its advice and suggestion, being the product of a finished chemist who knows the needs of the shop and school. Many an assayer would do well to follow the hints given in this book on sampling and preparation of samples.—*MINING AND SCIENTIFIC PRESS*, Sept. 19, 1908.

THE CHEMICAL ENGINEER is a monthly journal of *Practical, Applied and Analytical* chemistry published in the interests of Chemical Engineers, Chemists, Chemical Plant Superintendents, Mining Engineers and Metallurgists.

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No. 3.

THE WORK OF A MUNICIPAL GAS TESTING STATION.

By EDWARD K. HAMMOND.

(Continued from August issue.)

With the calibrations of the pentane lamp, the meter and the thermometers completed, the equipment is ready for use in making a photometric determination of the gas supply. For this test, the gas burner shown in Fig. 4 is mounted at the end of the table in the dark room, that was formerly occupied by the candle balance, when the lamp was calibrated. The socket into which this burner screws is shown on the table in Fig. 1. The meter through which the gas passes on its way to the burner is located at the opposite end of the table, beyond the pentane lamp, and connects with the burner by a pipe beneath the table. This meter is equipped with a clock attachment that enables the rate at which the gas is being burned to be determined. The rate is controlled by adjusting the pressure regulators so that the consumption of gas has been brought to practically 5 cu. ft. per hour. This is the normal rate for the average gas burner and the illumination standard of most city ordinances is based upon such a rate of consumption. The common practice in photometry is to use three pressure regulators to adjust the flow of gas to the burner. Two of these regulators are situated in the piping between the main and the meter, while the third is located between the meter and the burner. The first of the regulators between the main and the meter is of the dry type in which a flexible diaphragm allows the gas volume to adjust itself to compensate for fluctuations in pressure. The other regulator in front of the meter is of the wet type. It consists of an inverted bell, dipping into a water seal, which rises or falls with variations of the pressure of the gas passing through it. This regulator is suspended at the end of an arm which is counterbalanced with weights. By altering the number of weights used to balance the regulator, the pressure of the gas can be adjusted so that the desired rate is secured.

The meter through which the gas is burned for the photometric test has two indicators geared to it. The first dial merely indicates the volume of gas which has been burned. The second dial has two needles rotating over it about the same center. One of these

needles indicates the passage of gas through the meter; the other is on the clock attachment. The gas hand rotates twelve times for the passage of 1 cu. ft. of gas through the meter while the time hand rotates once a minute. By adjusting the pressure regulators, the flow of gas is brought to the standard rate, which is shown by having the two hands rotating over this dial in unison. Should it happen, however, that conditions alter during the test, thus throwing the gas rate slightly off, the necessary factor to correct for the effect



Fig. 4. Gas Burner Used For Photometric Tests.

which this deviation from the standard rate will have upon the illumination produced by the gas is easily obtained.

For ordinary purposes, a run of ten minutes is sufficient to enable the candle power of the gas to be accurately obtained, readings being taken at intervals of one minute. After taking the fifth reading, the sight box is reversed to compensate for any inequality in the readings taken on opposite sides of the disc, as explained for the lamp calibration.

For use in making a sample calculation, the average value of a set of ten readings recently taken by the

writer will be used. The average of these readings, as taken from the photometer bar, was 23.15 candle power. The gas burned slightly slow during the course of this test, the necessary correction factor to reduce the results to the light that the gas would have produced when burning at exactly 5 cu. ft. per hour

being $\frac{1}{0.996}$. In order to reduce the results to values

based upon gas volumes under the standard conditions of temperature and pressure, the relation between the volume of the gas under the conditions of temperature and pressure existing during the test, and what it would have been for the standard conditions of a temperature of 60° F. and a pressure of 30 ins. of mercury must be obtained. To avoid the necessity of calculating this relation from the laws of Charles and Boyle, tables have been arranged giving the necessary correction factor for the various temperatures and pressures occurring in laboratory practice. The temperature of the meter thermometer at the time of the test was 78.5° F. The reading of the meter manometer was 0.9 ins. of water and the barometer reading was 29.33 ins. of mercury. Converting the 0.9 ins. of water to inches of mercury and adding it to the barometric pressure gives 29.40 ins. of mercury as the total pressure of the gas. The temperature and pressure of the gas is now known and by referring to the table of

correction factors $\frac{1}{0.931}$ is found to be the factor cor-

responding to the conditions under which the test was made. Consequently, dividing by this factor converts the results obtained for the photometric test to what they would have been for gas under standard temperature and pressure conditions. The necessary data is now available for calculating the candle power of the gas as shown below:

$$\frac{23.15 \times 0.721}{0.931 \times 0.996} = 24.25 \text{ candle power.}$$

In the above calculation it will be remembered that 9.721 is the candle power of the lamp that was secured in the calibration against sperm candles, as previously outlined.

CALORIMETRIC TESTS.

A good arrangement of apparatus for making calorimetric tests of a gas supply with the Junker calorimeter is shown in Fig. 5. This arrangement enables the tests to be made with the greatest possible dispatch which is consistent with accurate results. It will be seen in the illustration that two receivers are used, one to collect the water flowing from the calorimeter and the other to act as a counter poise on the other platform of the scale. This scale is so situated that the receiver is placed beside the waste pipe leading to the laboratory sink, and at the completion of a test, the rubber tubing carrying the water away from the

calorimeter is merely switched from the receiver into the waste pipe.

The water used for the calorimeter is drawn from a supply tank suspended from the laboratory ceiling. This tank is filled with water from the main, immediately after a test has been completed. In this way, the water has reached a constant temperature before it is required for use. If it was attempted to use water direct from the main, it would be found that the fluctuation in temperature covers a range of several tenths of a degree, thus creating a tendency toward errors in the results of the determination.

For the benefit of those who are not familiar with the construction of the Junker calorimeter, a brief description will be given before passing on to the method of using the instrument. The gas to be tested is passed through the meter shown in the illustration; it then

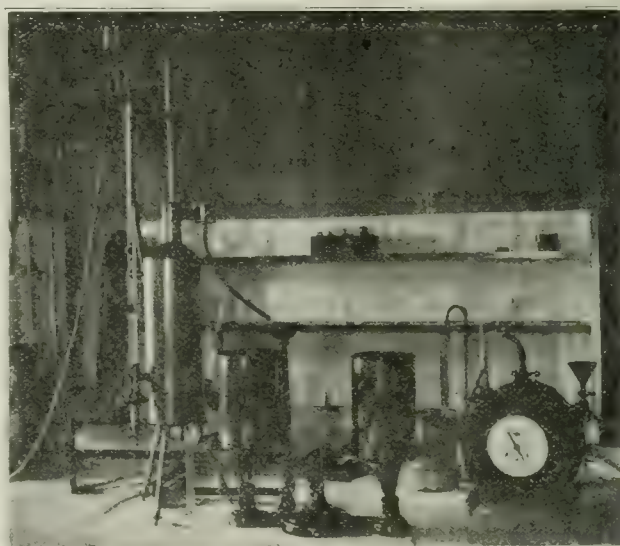


Fig. 5. A Good Arrangement of Apparatus for Calorimetric Tests.

passes through the wet pressure regulator, which is of the same type that was described for the photometer, and goes from this regulator to the Bunsen burner. The burner is clamped in the combustion chamber of the calorimeter, and the products of combustion rise to the top of this chamber, from which they pass down through tubes between the double walls of the instrument and escape through the stack shown at the right hand side.

In passing down through these tubes, the products of the combustion of the gas give up their heat to the water, which surrounds the tubes and flows from the bottom to the top of the calorimeter. The rise in the temperature of the water, brought about in this way, is determined by reading the two thermometers seen at the top and bottom of the instrument. Calling these temperatures T_1 and T_2 , respectively, the rise in temperature R is found by subtracting T_2 from T_1 . Thus,

$$R = T_1 - T_2.$$

The water leaves the calorimeter through the tube at the right and for the time of the test it is collected

in the receiver on the scale pan. It is then weighed to determine the weight M .

The flow of water through the calorimeter is kept constant by means of weirs in the small reservoirs on the tubes through which the water enters and leaves the calorimeter. At the left hand side, where the water enters, it flows into a circular weir from which it enters the inlet pipe of the calorimeter. The quantity of water supplied is more than the required amount and the surplus flows over the weir and escapes through the rubber tube leading to the sink. On the outlet side, the water escapes on the outside of the weir. When the level has risen sufficiently to reach the edge of the weir, it flows over and escapes into the receiver. This arrangement maintains a practically constant head of water and keeps the flow through the calorimeter uniform.

For use in making a sample calculation, the following data has been assumed:

1. Average value of $T_1 = 91.14$ } $T_1 - T_2 = 17.83$
2. Average value of $T_2 = 73.31$ } $F = R$.
3. Weight of water collected = 7.255 lbs. = M .
4. Volume of gas burned during test = 0.2 cu. ft. = V .
5. F = correction factor for temperature and pressure, as taken from the tables = 0.956.

Then the gross calorific value of the gas is

$$\frac{(T_1 - T_2) \times M}{F \times V} = \frac{R \times M}{F \times V} =$$

$$\frac{17.83 \times 7.255}{0.956 \times 0.2} = 677.0 \text{ B. T. U. per cu. ft.}$$

For all ordinary purposes, the combustion of 0.2 cu. ft. of gas is sufficient to enable accurate results to be obtained, and during the run a series of six readings of T_1 and T_2 are taken, from which the average values are secured for use in making the calculation shown above.

In burning gas in a Junker calorimeter the water vapor produced from the combustion of the hydrogen and hydro-carbons in the gas is condensed. During condensation, this water vapor gives up its latent heat of vaporization to the jacket water; the water runs out from the calorimeter through a small pipe provided for the purpose and is collected in the graduate shown at the right hand side of the calorimeter in Fig. 5. For each cubic centimeter of water vapor collected in this way 2.38 B. T. U. of heat has been liberated.

In the majority of classes of service for which gas is used for heating the water vapor produced from the combustion is not condensed and so does not give up its latent heat. Consequently, the heat which is derived from the gas under these conditions is less than the value determined in the calorimetric test by

the amount of heat which was derived from the condensation of the water vapor in the calorimeter.

If it is desired to secure the net calorific value of the gas, the amount of heat liberated by the water vapor must be subtracted from the gross value. In making this calculation, the amount of heat liberated from the water vapor is determined by multiplying the number of cubic centimeters collected in the graduate by 2.38. For the test under discussion 6.8 cubic centimeters of water was condensed. This gives the amount of heat derived from this source as $2.38 \times 6.8 = 16.2$ B. T. U. The net calorific value of the gas is then found to be $677.0 - 16.2 = 660.8$ B. T. U. per cubic foot. The net calorific value represents the amount of heat that is derived from the gas for average classes of service, consequently, the net value is usually reported.

VOLUMETRIC ANALYSIS.

Volumetric analysis plays an important part in supplying the gas works with data which is used to control the quality of his company's product. For the municipal gas testing station, the results of such an analysis are of value only in so far as they enable an idea to be gained of the quality of the gas supplied to different sections of the city. The lighting and heating properties of the gas are the points of primary importance to the municipal chemist, and he is able to gain reasonably accurate data covering these properties of the gas supplied in different sections of the city by bringing samples in to the laboratory and comparing the results of their analysis with those of gas samples taken from the laboratory supply pipes, where it has been possible to make simultaneous calorimetric and photometric tests.

In addition to the regular volumetric analysis, determinations are made in most municipal laboratories for the amount of sulphur and ammonia carried by the gas. The results of these determinations are of considerable importance, as most cities which maintain gas testing stations have provisions in their ordinances which limit the quantity of sulphur and ammonia, and which impose a penalty for anything over the maximum allowable quantity.

Figs. 6, 7 and 8 show the different pieces of apparatus used for the analysis of gas. They will be discussed in the order in which they have been referred to. The apparatus shown in Fig. 6 consists of a modification of the Hempel burette used for making the customary volumetric analysis; the apparatus in question having been developed and placed upon the market by the United Gas Improvement Company, of Philadelphia. The burette is surrounded by a water jacket, to preserve a uniform temperature, and is graduated for a capacity of 102 cc. of gas. At the top of the burette there is a bulb which holds about 60 cc.; the graduations range from 40 to 102, greater space and consequent accuracy being obtained in this way, owing to the greater amount of space which can be devoted to each 1 cc. graduation along the length of the burette.

Just above the bulb at the top of the burette, there is a five-way stop cock, which gives access to the absorption pipettes and to the manometer used for regulating the pressure of the gas in the burette. This manometer does away with the use of the leveling bottle for taking readings, as the gas is brought back to barometric pressure after each absorption by opening the connection in the five-way cock between the burette and the manometer.

In starting to introduce a sample of gas into the burette for analysis, the leveling bottle is raised until the burette is filled with water and an excess flows out through the rubber connection that is shown in the illustration holding the explosion pipette. The five-way cock is then turned to give access to the manometer; this allows the water to flow into the manometer, and when it is nearly filled, the leveling bottle is low-

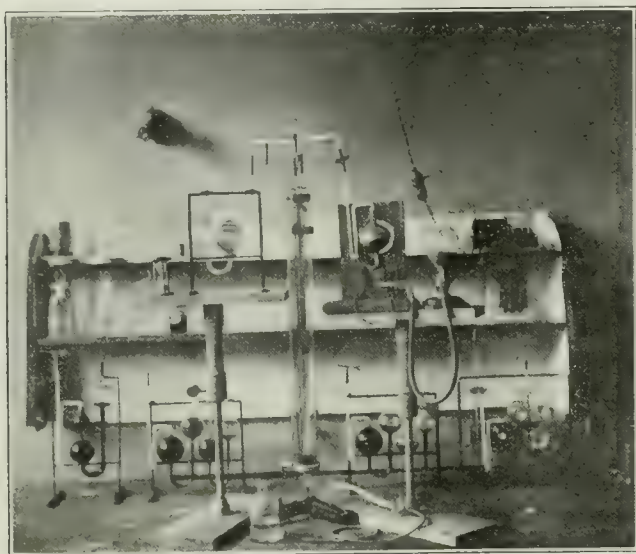


Fig. 6. Modified Hempel Apparatus for Volumetric Analyses.

ered until the level of the water in the right hand leg of the U-tube has dropped until the latter is about one-half full. The stop cock is then turned to shut off access to the manometer. The five-way cock is next turned to connect the potash pipette with the burette; the leveling bottle is then lowered to draw the potash over to the entrance to the burette. After the completion of these manipulations, it will be found that a small amount of air has been drawn into the burette. This air is expelled by opening the connection at the right hand side of the burette and then raising the leveling bottle until water flows from the connection.

The apparatus is now ready to receive the sample of gas for analysis, which is introduced through a rubber tube connected with the opening through which the water has just been expelled. When connection with the gas supply has been made, the burette cock is opened and gas is allowed to flow in until the water level has dropped to about the 102 cc. graduation; the cock is then closed.

In order to obtain uniform readings, a sand glass is

used to allow the same amount of time to elapse before taking the reading of the burette in all cases. This precaution ensures having the water drain off from the burette uniformly after completing each of the absorptions.

After the burette has drained for the specified time, as indicated with the sand glass, the five-way cock is turned to form a connection with the manometer. The leveling bottle is then raised until sufficient gas has been forced into the manometer to bring the level of the water in the two legs of the U-tube to the same height; the cock is then closed. The next step is to bring the gas in the burette to atmospheric pressure. To do this, the right hand side of the manometer tube is momentarily disconnected from the rubber tubing that secures it to the sealed tube in the water jacket that surrounds the burette. This allows the air confined in this tube to come to atmospheric pressure, and as the pressure of the air in this tube remains constant, the pressure of the gas in the burette can be brought to a constant figure, after each absorption, by opening the connection to the manometer and adjusting the level of the water in the U-tube. This is the next step in the analysis, the cock being opened and the level of the water adjusted in the manner described, after which the cock is again closed.

The volume of the gas in the burette now represents the quantity taken for analysis. If the directions are properly followed, this volume will be very close to 100 cc. and, as a consequence, each contraction represents the percentage of the constituent which has been absorbed.

The next step in the analysis is to absorb the carbon dioxide. To do this, the cock is turned to give access to the manometer and the gas in the U-tube is drawn over into the burette until the water just reaches the stop cock. The cock is then turned to connect the burette with the potash pipette, after which the gas is forced over into this pipette. The latter is then shaken to thoroughly wash out the carbon dioxide and the burette cock is next opened to allow the gas to be drawn back into the burette. The cock is next turned to give access to the manometer and the leveling bottle is then manipulated to bring the level of the water in the U-tube back to the required point. The cock is then closed and after the sufficient amount of time has been allowed for the water to drain from the burette, as indicated by the sand glass, the burette is read. The difference between this and the preceding reading shows the number of cc. of carbon dioxide which has been absorbed from the gas, this figure representing the percentage of this constituent which was originally present.

The same process is repeated for the absorption of the illuminants, oxygen, carbon monoxide, methane, and hydrogen. For the determination of the first three constituents, fuming sulphuric acid, potassium pyrogallate, and cuprous chloride are used. After absorbing the illuminants and carbon monoxide, the gas must

be passed over into the potash pipette, before taking the reading of the burette, in order to wash out the acid fumes which have been carried back.

In determining hydrogen and methane, about 15 cc. of the gas which is left after absorbing the other constituents is passed over into the potash bulb; the remaining gas is then expelled from the burette. About 85 cc. of air is next drawn into the burette and the gas stored in the potash bulb is then mixed with the air in the burette. This mixture of gas and air is then forced over into the explosion pipette, which is shown connected up ready for use in Fig. 6.

In making the explosion, it is important that the rubber connections at the top of the pipette are wired in place, also that this connection is closed with a screw clamp at the time that the explosion is made. If these precautions are not taken, the pressure set up by the explosion is likely to force the connections loose and spoil the determination. The cock at the bottom of the explosion pipette should also be open so that the shock may be taken up by forcing mercury over into the reservoir.

Fig. 6 shows a convenient arrangement of apparatus for making the explosion. It will be seen that a small transformer is used, which allows current to be taken from the lighting circuit; this transformer is kept permanently connected with the spark coil as shown. To prepare for the explosion, it is merely necessary to bring the leads from the coil and connect them with the binding posts on the explosion pipette, from which wires run to the platinum tips sealed into the glass at the top of the bulb. This arrangement has the further advantage of avoiding twisting off the platinum connections, an accident which is likely to occur when the leads from the spark coil are connected directly to them.

With the apparatus properly arranged, a piece of fine wire mesh is placed in front of the pipette to provide against accidents in case the glass should burst. The switch on the lamp socket is then turned on and off again, thus throwing a spark through the explosive mixture of gas and air in the pipette and causing it to explode. The wires are now disconnected from the pipette and the screw clamp is released from the connection at the top of the pipette. The five-way cock on the burette is then opened and the mercury reservoir raised, thus forcing the gas back into the burette. This gas is next brought to atmospheric pressure by adjusting the manometer, and after the water has had sufficient time to drain from the sides of the burette, the reading is taken. The gas is next forced over into the potash pipette to wash out the carbon dioxide which was formed from the explosion of the methane; it is then returned to the burette and after adjusting the pressure, the reading of the burette is taken.

The August output of the Lake Superior copper mines is estimated at 18,173,000 lbs. of refined copper, a decrease over the output during the same period of 1911.

SURFACE COMBUSTION.*

By H. C. BLACKWELL, DAVENPORT, IA.

Many of us who were able to attend the convention of the American Gas Institute, at St. Louis last October, were immensely interested in a very instructive and well delivered lecture on "Surface Combustion," by Prof. Wm. A. Bone of Leeds University, England. I was not in a class by myself in leaving St. Louis feeling that Prof. Bone had made a wonderful discovery, and that some of our present methods would prove antiquated as soon as his ideas could be put into practice. I was greatly surprised when I read in "Progressive Age," Feb. 15th, that C. E. Lucke (December, 1901) presented to the American Society of Mechanical Engineers the same ideas as those of Prof. Bone. Mr. Lucke performed his experiments in 1900 while investigating the heat engine problem.

In placing this subject before the American Gas Institute, Prof. Bone laid special stress on the fact that heretofore it had been considered, in industrial heating operations, that contact of flame with surfaces should be avoided; this idea being in direct opposition to the theory of surface combustion. The conclusion reached is that hot solids possess the power of accelerating the combustion of an explosive gas with its proper proportion of air for complete combustion, the combustion taking place without flame.

First.—A burner to make use of these ideas must consist essentially of a number of surfaces of a highly refractory material contained in a suitable chamber; and, second, an injector for supplying a suitable mixture of gas and air. This, as well as any other burner using an explosive mixture of gas and air, must necessarily be designed to prevent backfiring, which might be accomplished in three ways:

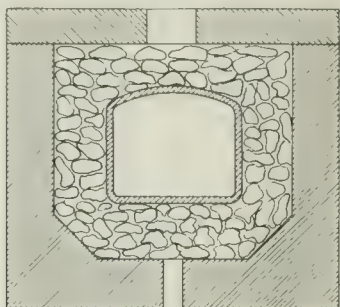
1. By using a tube so small in diameter that the flame could not strike back.
2. By using wire gauze screens.
3. By causing the mixture to flow into the combustion chamber with a velocity always greater than the rate of propagation of flame. Of the three means mentioned only the last is practicable; for, with the first, only a limited amount of gas could be burned; and, with the second, the entering mixture would be fired as soon as the gauze became hot.

A burner utilizing the principles of surface combustion may be so varied in design as to be applicable under widely different conditions. Extremely high temperatures are easily obtainable with this process, and it now appears that gas can be used where heretofore it was impracticable and uneconomical. For economic heating atmospheric burners may be used through only a small range of temperatures, up to about 650° F. Blast burners have made it possible to reach 3,200° F.; but with this process, providing

*Paper prepared for the Eighth Meeting, Iowa District Gas Association.

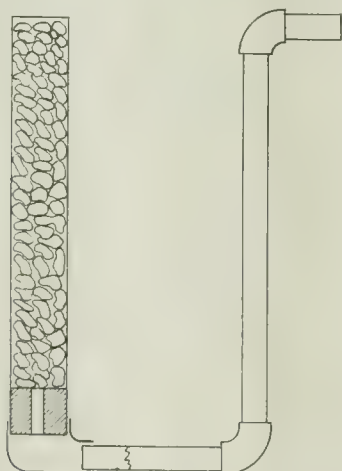
as it does a concentration of heat, and a much higher efficiency, as well as making temperatures above $3,400^{\circ}\text{F}$. obtainable, the industrial gas field should be greatly widened.

In the application discussed by Prof. Bone we have the heating of crucible and muffle furnaces, by surrounding the crucible or muffle with crushed firebrick or other refractory material, meshed to a suitable size.



Muffle Furnace.

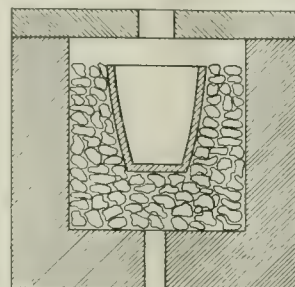
the mixture burning in contact with these surfaces: also lead melting, by having the burner in a hot bath of lead, the gas burned serving to keep the lead well above the melting point, melting more lead as it is added. Also, the steam and hot water fire tube boilers, where the tubes are packed with crushed firebrick the gas being burned in the tubes. These types of boilers, when worked out and adapted to meet existing conditions, should find many applications. The



Heater for Lead Baths.

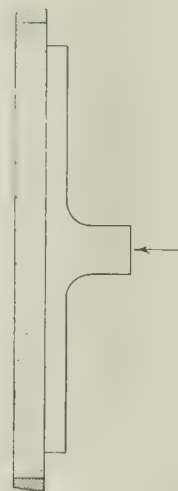
diaphragm burner, where the gas is burned without flame on the surface of a porous refractory diaphragm, should meet with favor by reason of the precision with which temperatures may be maintained, and economical consumption of gas, together with a great concentration of radiant heat. The burner itself is made up of a block of porous, refractory material, built into a cast or sheet iron back, into which the mixture of gas and air is introduced. According to Prof. Bone these burners, after long usage, show no signs of deterioration; and they should not, as the only part affected by use is the heated surface of the porous block.

In connection with diaphragm heating it might be well to call to mind a few fundamental principles in regard to heat. As you all know, heat is transferred in three different ways, namely: Radiation, convection and conduction. Of these the last two contribute the most to the heat losses, that we commonly meet with, and if we received heat by radiation only our losses would be greatly reduced; so it is with surface com-



Crucible Furnace.

bustion, and more particularly with diaphragm heating. These diaphragms are so constructed that they are portable, consequently we have a portable burner with intense radiative power that may be used for a great variety of purposes. In starting this burner and proportioning the mixture for perfect combustion, the flame retreats on to the surface and then, becoming incandescent, the flame disappears and leaves a radiant,



Diaphragm Burner.

glowing surface. Temperatures may be obtained and maintained with this burner up to $1,550^{\circ}$, according to the rate of supply of the mixture.

I have here a burner very similar to the one used by Bone in his lead melting surface. It consists of the pipe, as shown, and a fire-clay plug, with suitable orifice in the bottom of the last leg, the remainder up to the top being filled with crushed firebrick. This tube is in itself sufficient to fully illustrate the principles of surface combustion in a bed of refractory material, more particularly as applied to boilers. By starting it we find that, as the brick becomes hot, the mixture being properly proportioned, the flame strikes

back to the entering orifice, but it cannot pass the orifice, however, because the velocity of the entering mixture is greater than the speed of the propagation of flame, and the gas is burned just as it expands into the region of lower pressure in the pipe containing the broken firebrick. The brick quickly becoming incandescent, the red band around the pipe shows very plainly just where the combustion is taking place. It is seen that the generation of heat takes place in a relatively small place, that the pieces of crushed firebrick in the rest of the tube serve as baffles, and the gas is relatively cooled when it leaves the tube.

Here is a miniature steam boiler, in construction similar to the one described by Prof. Bone, utilizing the principles of surface combustion. It is exactly the same as the one just described, save that the tube is surrounded by an outer casing which is partially filled with water. We see how quickly the water is raised to the boiling point.

I have here another device which will illustrate to some extent the appearance of the chamber in which surface combustion takes place. This is a 4 by 2 reducing coupling, with a plug, having a suitable orifice in the 2-inch pipe, the rest being filled with broken firebrick and it may be possible with it to further illustrate the performance of flame in contact with hot surfaces.

To sum up, then, in surface combustion, we are able to burn a large amount of gas in a limited space, and the calorific power of the gas being transformed into radiant heat, a much greater efficiency than heretofore obtainable, and higher temperatures are possible; all this without elaborate apparatus. Though what little work we have done at Davenport has been largely of a preliminary nature, we are nevertheless able to see some of the possibilities of this process and believe that it will in different ways be brought gradually into use and tend toward a greater development of the gas industry.

The mine production of gold in South Carolina in 1911 was 987.24 fine ounces, valued at \$20,408, according to H. D. McCaskey of the U. S. Geological Survey, a decrease in value of \$17,916 when compared with the 1910 production. The small silver production of 11 fine ounces valued at \$6 was 35 fine ounces less in quantity and \$19 less in value than in 1910. The total value of the gold and silver output was \$17,935 less than in 1910. The yield of gold and silver in 1911 was reported from 6 placers and 3 deep mines against 10 placers and 2 deep mines in 1910. The total quantity of ore from the deep mines in 1911 was 9,302 tons all siliceous gold ore with an average recoverable value of \$2.17 ton. The placer output in 1911 was very small, only amounting to 12.63 fine ounces.

The total production of manganiferous ores in the United States in 1911 was 522,357 long tons, as compared with 619,735 tons in 1910.

TRUE CONSERVATION.

In the preface to Bulletin 47, Notes on Mineral Waste, written by Charles L. Parsons, chief mineral chemist of the Bureau of Mines, which has just been issued, Dr. Joseph A. Holmes, the Director gives his views upon what he terms real or true conservation. Dr. Holmes says: "During the past year, in producing 500,000,000 tons of coal we wasted or left underground, in such condition that it probably will not be recovered in the future, 250,000,000 tons of coal; we turned loose into the atmosphere a quantity of natural gas larger than the total output of artificial gas during the same period in all the towns and cities of the United States; we also wasted or lost in the mining, preparation, and treatment of other important metal-liferous and non-metalliferous minerals from 10 to 15 per cent of the year's production of such minerals. These losses serve to indicate the importance of inquiries and investigations by the Federal Government for the purpose of lessening the waste of essential resources—investigations on the same general lines as those looking to a reduction in the loss of life in the mining operations of the country and the far more extensive investigations looking to the more efficient production and use of agricultural products, both of which are being conducted by the Federal Government.

"In a consideration of the possible activities of the individual, the state and the Federal Government in behalf of a less wasteful use of our mineral resources certain facts and principles should be kept clearly in mind, namely:

"That the present generation has the power, and it will exercise the right, to use as much of the country's resources as it actually needs; there can and there will be no such thing as stinting the present generation by bottling up resources for the use of the future.

"That the Nation's needs are not likely to be curtailed; these needs will increase with the extent and diversity of the Nation's industries, and they will increase more rapidly than population increases, for the reason that the per capita consumption of mineral products is rapidly increasing and that the men of this generation will not mine, extract, or use these resources at continuous financial loss to themselves in order that something may be left for the use of future generations; there can be no such thing as a mineral industry without profits.

"Furthermore, it should be clearly understood that the mineral resources of this country have required long ages for their accumulation and that of these resources the Nation has but the one supply. There are no known substitutes available to meet the Nation's further needs when that supply will be exhausted and, to the best of our present knowledge, this one supply must serve as a basis for both the needs of the present and the far greater needs of the future.

"In a higher way our mineral resources should be regarded as property to be used and to be held in trust with regard to both the present and the future needs of the country. It should be remembered that neither human labor nor any human agency has contributed to their origin or to their intrinsic value, and that whatever rights the individual may possess have been derived from the General Government and from the state as the original owner. The state does not surrender its right, and should not neglect its duty to safeguard the welfare of its future citizens by preventing the wasteful use of these resources. Though the individual may claim the right to use the resources in proportion to his needs and the needs of the community, he certainly has no right to waste that which is not needed for present use but is certain to be needed hereafter.

"Those in charge of the investigations of the Bureau of Mines recognize the rights and duties of the Federal Government as being limited to the carrying on of inquiries and investigations with a view to determining the nature and extent of this waste of resources, the means by which it may be diminished, and the setting forth of the facts in the case.

"The present report embodies the results of certain preliminary inquiries as to the nature and extent of this waste. It will be followed by a more detailed report on the subject as soon as the necessary inquiries and investigations have been conducted and the results put in shape for publication.

"In the preliminary work along these lines the representatives of the bureau have received the cordial co-operation of the engineers and chemists associated with the varied mineral industries of this country and also of the owners and the operators of the mines and the metallurgical plants."

The mine output of gold, silver, copper, lead, and zinc in California in 1911, according to Charles G. Yale, of the United States Geological Survey, was valued at \$25,174,677, a decrease of \$1,845,728 from the corresponding value for 1910, although the production for 1910 included no zinc. The total decrease was due mainly to a curtailment in the output of copper because of litigation over the smelter-fume question. The mine production of gold in 1911 was \$19,738,908, an increase of \$23,468. The output of silver was 1,270,445 fine ounces, valued at \$673,336, a decrease of 569,640 ounces in quantity and of \$320,310 in value. The production of copper was 36,316,136 lbs., valued at \$4,539,517, a decrease of 12,384,620 lbs. in quantity and of \$1,645,479 in value. The output of lead was 1,398,111 lbs., valued at \$62,915, a decrease of 1,472,866 pounds and \$63,408. The output of zinc, however, none of which was produced in 1910, was 2,807,035 lbs., valued at \$160,001.

The production of clay-working industries of the United States in 1911 was valued at \$162,236,181.

PEAT BRIQUETTING.*

By G. J. MASHEK.†

The briquetting of peat for fuel purposes, as I gather from reports and statistics, appears to be an old art. In spite of all the work that has been done in this direction in Europe, where many similar undertakings on the continent apparently have been commercially successful, nevertheless from all reports of effort made to briquet peat in North America, all appear to have been more or less of an experimental nature. There are large deposits of this material in many parts of this country and in Canada, where coal is high, so that it would appear that at least in such localities briquetting of peat would be commercially successful; but from best reports obtainable this does not seem to be the case.

The difference between the success of peat briquetting in Europe and America evidently is due, first, to the low cost of labor on the other side, and second, to the low price at which high-grade coal can be obtained in this country. The briquetting of peat in the United States and Canada will undoubtedly have to be worked out on the same lines that the briquetting of coal has gone through. As stated at the outset, the method of handling peat and briquetting it has been worked out in Europe so that good, substantial machinery can be obtained to do this work over there. This same machinery, however, when imported into this country, does not seem to meet the requirements, and the cost of operation is always higher than the value of the product turned out. This has also been, until within recent years, the history of coal briquetting in this country, although in Europe this is an established business of large magnitude; and yet, of all the equipments that have been imported from Europe into this country, none have been commercially successful. As the result of these failures it was found necessary to develop suitable machinery and processes designed to meet our conditions in order to produce coal briquets acceptable to the American trade. It was learned, in the first place, that the briquets must be considerably better than any of those produced in Europe; second, that they must be produced cheaper, especially as far as labor is concerned, and third, the briquets must be of more suitable sizes and of better quality to compete with domestic coal.

While we have not gone deeply into the briquetting of peat, although we have spent a good deal of time and money in developing machinery and processes for the briquetting of coals, we have equipped one peat briquetting plant to produce high-grade briquets. Although this plant was built more for experimental purposes than anything else, it produced a very high-grade fuel, both when straight peat, thoroughly dried out, was used, and also with a mixture of about 80

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per cent of peat and 20 per cent of coal dust; this made briquets practically equivalent to ordinary anthracite coal. While the pure peat briquets were a little lower in heat units than the mixed ones, the effective heat obtained from them during combustion was equally as great.

I will not enter into the discussion as to the best method of recovering the peat from the bog, as there are several methods of doing this work and machinery for them perfected. The particular process most suitable in a given case will depend altogether on the quantity of raw material desired per day and on the location, size and nature of the bog. As stated before, this part of the business is apparently fairly well developed and improvements in minor details will be made as the business is developed.

In my opinion most of the errors and failures of the past have been made in the method of extracting the moisture from the peat. A certain percentage of this moisture, say down to about 50 per cent or 60 per cent, may satisfactorily be extracted by ordinary drainage and, to some extent, by air drying. After this point is reached, any turning over or handling of the material to dry it further in the air, necessarily must be expensive on account of the labor involved. It is at this point that a radical departure from the present methods must be adopted, and on account of the high cost of labor on this continent this further drying will have to be done automatically by machinery.

While all are familiar with the ordinary rotary dryers, which will evaporate only from 6 to 7 lbs. of water per pound of fuel used, this method is entirely out of question for drying peat on account of the large consumption of fuel. Therefore if the drying is to be done at a low cost a more economical and modern method will have to be adopted, one that will remove anywhere from 20 to 40 lbs. of water from the peat per pound of fuel fired. This result can only be accomplished by machinery such as is used for evaporating water from salt, sugar, etc.; that is, by using a large rotary dryer which is provided with lifting shelves so as to spray or drop the material from top to bottom in a divided state. Through this sprayed material a current of hot air should be passed, preferably by means of a positive blower, which will remove the water, not by evaporation, but by absorption; before going to the drier, the air should first be sent through a preheater so designed that it will take up practically all the heat from the furnaces, the preheater being arranged so that the air will pass through heated brick checker work or around staggered tubes, the inside of the tubes carrying the products of combustion from the furnace.

An efficient dryer of this description has been developed by the General Reduction Gas Co. of 49 Wall St., New York, and if a machine of this kind is used to dry peat, it would dry it at about one-quarter the fuel cost of the present methods in use.

The drying ought to be carried on until the remain-

ing peat contains about 10 per cent, or less, of moisture. The peat at this point is still not in the most suitable form for briquetting, for the reason that it is brittle and requires a binder of some kind to hold it together. If, however, any kind of binder is used, whether it is a sodium silicate, waterproofed flour, sulphite pitch or coal tar pitch, the cost of briquetting, including all labor, fuel and binding materials (exclusive of the cost of peat) will run from \$2 to \$3.50 per ton, depending on the location of the plant. If even then the manufacturer would charge only a reasonable profit on the manufactured product, the price of the peat briquets would still be too high in comparison with coal in all but those sections of the country distant from coal mines, for the reason that the peat briquets will have anywhere from 6,200 to 8,000 B. t. u.'s per pound, as against coal of 13,000 to 14,000 B. t. u.'s per pound. In addition, they will burn very rapidly, possess very little advantage over ordinary wood and require considerable labor and attention to keep the fires going. The result of these factors is that in almost all cases it will be cheaper and more desirable, especially for domestic use, for the people to buy coal, as no matter how low a grade of coal it may be, it still would be better fuel than the peat briquets and could be had at about the same cost, when heat units are considered.

With the development of coal-burning furnaces, improved means of transportation, and the lowering prices of coal at distant points from coal mines from year to year, it is doubtful if peat briquets made under the conditions mentioned can compete with coal in any but the most isolated places, especially for steam-making or power-generating purposes.

For the reasons given I have arrived at the conclusion that it is entirely out of question to briquet peat in its natural state, especially when we know from analysis and tests that have been made, that, by retorting the peat in by-product coking ovens, valuable by-products such as tar, wood alcohol, acetate of lime and ammonia may be obtained and the peat carbonized or reduced to charcoal of high heat value. It is then an easy problem to briquet this charcoal dust, either alone, or after mixing with it from 10 per cent to 20 per cent of coal dust or slack, which usually can be obtained at from one-quarter to one-half the cost of ordinary coal.

I am informed by reliable authorities that the market value of the by-products from charring peat, exclusive of charcoal dust, will range from \$6 to \$8 per ton of dry peat, which is a larger return than peat will bring in almost any other form in large quantities, and, in addition, there is the peat charcoal dust, the most desirable material for the manufacture of high carbon briquets, which will bring an additional profit of from \$3 to \$5 per ton above costs of briquetting.

The addition of coal dust or screenings to the peat carbon dust makes a briquet that is almost as high in heat value as anthracite coal. The coal dust has the

effect of retarding the rapid combustion of briquets when made of charcoal dust alone. Briquets produced in this manner are low in ash, will not produce clinker in the furnaces, and weigh considerably more per cubic foot than the raw peat briquets, so that it is an easier matter to store and deliver them, and make a fuel that is superior to charcoal, or in fact, to any coal.

There is no necessity of developing any special machinery for briquetting carbonized peat, as ordinary coal briquetting machinery will handle this material to perfection. This process of utilizing the peat so that everything of value is obtained out of it and the material reduced to its most desirable state, is, in my opinion, the solution for the development of the peat industry.

While a plant to do this work as described above will call for a considerable outlay of capital at the beginning, I am confident it will be a paying investment right from the start, if installed on peat bogs that are situated where the cost of coal is high. By adopting this process and getting all the by-products from the peat, which will pay a good profit on the operation, the carbonized peat dust will be obtained for practically nothing. It has very little value except for manufacture into briquets, and for this purpose it is not excelled by any other carbon material.

The cost of briquetting this carbonized dust, including all labor, wear and tear, binder, interest on capital invested, and other fixed charges, should not exceed \$1.60 per ton in a plant capable of producing at least 10 tons of briquets an hour. Adding to this 20 per cent of 60 cents' worth of coal dust, valuing it at \$3 per ton, and 80 per cent of carbonized peat, allowing, say, \$1 per ton to the by-product plant, making the cost of peat \$0.80, this would make the total cost of the briquets in the bin ready to ship \$3 per ton, which is amply on the safe side. There should be no difficulty in obtaining from \$5 to \$8 a ton wholesale for the briquets in almost any part of this country and Canada where there are large peat bogs located at some distance from coal mines. By experience I have found that fuel made in this way will be preferred and give better results than the best quality of Pennsylvania anthracite coal.

Such briquets can be made smokeless by using as a binder sulphite pitch, a by-product from the manufacture of wood pulp, and of which there are unlimited quantities with practically no market for it. This material in its natural state is not waterproof, but can be made so at very little expense.

Sodium silicate, waterproofed by any of the well-known methods, is another desirable binder. This also produces an entirely smokeless briquet, although the ash content of the briquets will be increased from 3 per cent to 5 per cent, depending on the specific gravity of the carbonized peat dust.

Coal tar pitch or asphaltum can be used, but these materials usually are quite expensive, especially if these binders have to be shipped some distance from

the producing point, and they do not make an entirely smokeless briquet. Some objections may be raised by the users to the small amount of smoke produced from the burning of pitch or asphalt binder, which is produced immediately on ignition of the briquets and lasts about ten to fifteen minutes. This smoke or fumes can be entirely eliminated by passing the briquets through a special oven and distilling off the lighter volatiles of the pitch, which produce the smoke. The additional cost of this operation will not exceed 30 cents per ton.

The briquetting plant will be simple, for the reason that no dryers or preheaters would be required. All that is necessary will be a mixer, briquet press, binder handling appliances, power transmission machinery, and an oven if pitch or asphalt is used as a binder. It is impossible to give off-hand the cost of installation of such an equipment as that described, to apply to all conditions, for the reason that these conditions will vary so greatly and must be taken into consideration in making an estimate.

One thing that must be borne in mind in briquetting any material on this continent, is that briquets must be made of a size that will produce the best results in the fire. This is a very important item, as a size suitable for steam-making purposes would not answer for domestic use, and peat briquets are primarily a domestic fuel and necessarily too high in cost to compete against coal or other fuels for steam making or power purposes. The briquets must be of such size and shape that they will spout, and can be shoveled and handled the same as ordinary coal.

Another point that I wish to draw your attention to is that a high-grade briquet of this description must be waterproof and be capable of absorbing a very small amount of water, if any. Under the methods in vogue on this continent it is practically impossible to transport and deliver fuel in large quantities without the danger of getting the fuel wet, either in cars or in delivery wagons. The process described above will produce briquets that are waterproof and practically impervious to moisture.

Most of you are familiar with or have seen peat briquets, and know that in practically all cases the briquets are either square, rectangular or cylindrical in form, weighing anywhere from 10 ozs. up to several pounds. Fuel in this form is readily accepted in Europe, where the people have been brought up to use it in these sizes and are accustomed to break it into smaller and more suitable pieces to obtain the best results from it in stoves and furnaces. In transporting briquetted fuel in cars to Europe, the briquets are usually carefully stacked up, involving a large amount of hand labor.

This method of handling and transportation is entirely out of question in this country or in Canada, for the reason that labor is so high priced. The fuel in this form cannot be spouted and handled by the present appliances, which would run the cost of the fuel

too high on account of the handling expense, and there are very few consumers, even among the poorest, who will go to the trouble of splitting up and chopping the large sized briquets into smaller pieces, with the resultant dirt and labor, especially when they are asked to pay a high price for a strictly high-grade fuel.

In order to compete in the market here, therefore, it is necessary to produce briquets of the same size and grades as the prepared sizes of coal now being sold for domestic purposes. I have found the best size for peat charcoal dust briquets to be from $2\frac{1}{4}$ to $2\frac{1}{2}$ ozs. in weight. The fuel must burn and behave in the fire like high-grade coal; life is too short to introduce a fuel that requires special training and special handling in order to obtain the best results.

Briquets placed as described, with the drafts properly regulated and set, weight for weight will burn the same length of time as high-grade semi-anthracite or anthracite coal, and there is no difficulty whatever in keeping a fire overnight, even in ordinary kitchen stoves.

Another point to which I wish to call your attention is that there is nothing experimental or untried in any of the equipment proposed, as, for instance, there is nothing experimental or untried in the method of recovering the peat from the bog and storing it. These methods, as explained, may differ, and care must be exercised in selecting the most suitable type of equipment to suit the nature and size of the bog and the amount of peat desired per day.

There is nothing new or untried in the absorption dryer. This class of machinery is developed beyond the experimental stage, and there are responsible corporations willing to guarantee the evaporative efficiency of these machines, whether it is desired to dry peat for the by-product retorts or for other uses.

The next step is the by-product or carbonizing plant. This also is not an experiment or an untried process, as there are a number of manufacturers in the country building apparatus of this kind, who are willing to put in apparatus guaranteeing the recovery of practically any by-products that peat may contain. This is done with sawdust, wood, sugar cane and other kinds of plant materials where the recovery of the by-products offers a satisfactory return, and by-product ovens or retorts, either of the chamber or continuous type, can be utilized for this purpose.

The last step of briquetting the carbonized or charred peat is a simple problem, for the reason that the same machinery and equipment that are used for briquetting coal will make first-class briquets of this materials, and there are manufacturers who stand ready to guarantee the capacity and cost of this part of the operation.

The problem therefore resolves itself down to a question of sufficient capital and a proper location, in order to make this business a commercially successful enterprise right from the start, and if this undertaking is engineered properly and if substantial construction

and equipment are used throughout, the plant will pay anywhere from 25 per cent to 50 per cent annually on the capital invested, and in addition to the volatile by-products, produce a fuel that will command a higher price in the open market than the best Pennsylvania anthracite.

Propositions of this kind have been brought to me on several occasions, but it was always with the idea of installing as cheap machinery as possible in order to make a showing, no matter of what kind, with the sole object of selling stock, so that it always was a foregone conclusion that the business would be a failure, and this, as a rule, is never discovered until after the stock is all sold and the promoters make their profit; matters of this kind always give a set-back to the development of any new industry.

I have not gone even into the approximate costs of a plant of this description, for the reason as stated, that conditions vary so much that it is practically impossible to give off-hand figures that would hold in all localities as local conditions must be taken into consideration.

While the method that I am proposing for the utilization of peat is probably not new to those who have made a study of this question, the plan is simply going a little deeper into the subject with the hopes that others will look into it still deeper with the idea of developing the peat industry into a paying proposition, instead of such experiments and trials as all the efforts in this direction in the past seem to have developed into. I have yet to see any reports of any firm or corporation engaged in the recovery of peat for fuel purposes that has declared a dividend. While the declaration of dividends is not the only mark of success, especially in the development of a new industry, it is an absolutely sure and a satisfactory sign.

According to an official report the quantity of pulp wood manufactured in Canada in 1911 amounted to 672,288 cords, or 73,801 cords more than in 1910. The value of this wood also increased, being \$4,338,024, against a value of \$3,585,154 in the preceding year. The value per cord, \$6.45, was higher than it has been for years.

Of the total consumption in 1911, the Province of Quebec, with its 28 mills, consumed 58 per cent of the entire output. The Province of Ontario had the largest consumption of pulp wood per mill, 12,450 cords. New Brunswick mills were hampered last year by low water, but notwithstanding the drought its four mills consumed 45,824 cords, or more than twice the province's consumption in 1910. Nova Scotia mills used only 22,221 cords. Of woods utilized in manufacturing wood pulp in the provinces mentioned, Quebec uses spruce, balsam fir, hemlock and poplar; Ontario and Nova Scotia the same species, with the exception of hemlock; while New Brunswick uses only spruce and balsam fir. The total exports of wood pulp from the port of St. John to the United States for the calendar year 1911 were valued at \$378,515.

METALLURGY

PLATINUM.

During the last 18 months the value of platinum has risen to the highest level it has ever attained, and with slight fluctuations, has maintained this level. A former high record occurred during December, 1906, when the quotations were \$38 to \$40. The more recent values have been the following: 1900, \$9.20 per ounce Troy; 1905, \$21.68; 1910, March, \$29-\$34.50; 1910, September, \$34-\$36; 1911, March, \$41-\$43; 1911, September, \$44-\$46.50; 1912, March, \$46-48.50; 1912, August, \$45.50-\$47.

There can be no doubt that the increase in the value of the metal is entirely due to the very large demand and the diminishing ore reserve. The main supply comes from Russia, where the cost of placer mining is increasing. The high prices have induced miners in Colombia, South America, which was the chief source before the Rusian deposits were known, to make increased efforts to improve their output, with marked success. Thus, the exports of platinum from Colombia to Great Britain which were nil in 1907 and only \$1,444 in 1909, increased to \$48,380 in 1910 and \$183,450 during 1911. Only a very limited quantity of platinum is produced in the United States, and is mainly derived as a by-product from working gold placers, mainly in California and Nevada, as detailed below.

The output of platinum from Russia is officially given as 175,716 ounces Troy during 1910, and the export as 6,871 kgms. during 1911. The metal is found in six localities and the respective output for 1910 show in what proportion: Tcherdyn, 6,350 ounces; Peru, 46,000 ozs.; South Verchotur, 110,824 ozs.; North Verchotur, 11,570 ozs.; South Ekaterinburg, 970 ozs.; North Ekaterinburg, 2 ozs. The output was over 11,500 ozs. greater than 1909 and 19,000 above that of 1908. The outputs of the three districts, Tcherdyn, North Verchotur and South Ekaterinburg are falling off and those of Peru and South Verchotur are increasing. The increase of value mentioned above has had a marked affect on Rusian enterprise, thus the poorer placer deposits which could only be worked at a loss with low prices and had been abandoned, have now been again opened and are producing the ore. The official outputs given above are by no means the whole, considerable quantities, estimated at more than 50 per cent, are sent out of the country without being recorded.

Geological experts state that all the more productive placers are derived from dunite, a kind of olivine, which occurs in the Urals in a rather narrow zone, wherever the parent rock has been located. The

placers suggest an alluvial origin; the average yield is a very small one, only 0.07 oz. of the crude metal is obtained from a ton of gravel, formerly the percentage was higher. Occasionally richer areas are found.

The most conveniently situated placers have been exhausted and those in outlying districts, or involving difficulties of working have to be taken in hand. So long as the present high prices continue the extra cost of working is not felt. The districts within which platinum is found have been so carefully surveyed that it is improbable that additional placers will be found. Some areas have been worked for over 70 years. There are possibilities in the Northern Urals, where the olivine has not yet been studied, and there are areas which have not yet been even visited. Improved and more modern system of working is being introduced into the Russian platinum mines, dredges are now used as well as excavators. The government is considering steps to prevent the secret production of crude platinum, so as to concentrate all the ore in its own hands. Up till the present, the platinum producers have never succeeded in limiting this poaching which has assumed colossal dimensions. The crude platinum found in Russia is refined in Germany, France and Great Britain; but the Rusian government is anxious to establish its own refineries, so as to put platinum on the market in the same irreproachable purity as is done by refiners in Western Europe. The fear has been expressed in Russia that the high price of platinum may induce a search for substitutes, but the properties of the metal are so exceptional, that it is extremely unlikely that a suitable substitute can be found.

The Rusian output of platinum from 1900 to 1911 both inclusive, has been as follows:

	Kgms.		Kgms.
1911.....	5,805	1906.....	5,770
1910.....	5,473	1905.....	5,257
1909.....	5,112	1904.....	5,031
1908.....	4,876	1903.....	6,010
1907.....	5,379	1902.....	6,127

The increase of value is well shown by the larger outputs of 1906 and 1911, but the still larger outputs of 1902-1903 suggest the gradual exhaustion of the deposits. The difference between the quantity given above as exported and the output during 1911 may be accounted for by the sale of reserve stock tempted by the high price. The impure platinum found in Russia contains about 83 per cent of metal, the other ingredients are mainly other metals of the platinum group of which palladium is the principal, also osmium and iridium, in all six metals. The crude one also contains some gold, which can be separated by amalgamation and there are also iron and chromite.

For the extraction of the pure metal there are two small factories in the capital, but they only deal with about 200 kgms. yearly, the bulk of the refining is done in Western Europe. American supply is mainly obtained from Germany and France, but the limited platinum output of the United States is refined in America.

There is no difficulty in separating the platinum metals from the minerals with which they are associated; but one of the most difficult problems the chemist has to solve is the separation of the individual metals of the platinum group from each other. They are very similar in their characteristics. Exact separation are necessary for even small admixtures may strongly effect the technically important qualities of the entirely pure platinum metal desired, for instance a minute addition of iridium would make platinum considerably harder. The first step at the refinery is to obtain the metal from the ore, the six platinum metals have then, so to say, to be disentangled. Important uses have been found for each and their value is even greater than platinum, as the supply is so much smaller. There are two methods of separation: The dry and the wet, the former is a smelting process, by the latter the ore is dissolved. It is the system now generally employed. The dry system has been discarded as it does not yield a perfect separation; it was largely used fifty years ago by the well known experts Deville and Debray, who were pioneers in platinum metal chemistry and the technical details of refining them. In the wet process the various stages follow the usual methods employed in making an analysis in the laboratory. The details in which many variations may be introduced are, of course the carefully guarded secrets of the refineries. Broadly, they may be described as follows: By a treatment with aqua regia the largest part of the precious metals is dissolved; the residue contains besides sand the alloy osmium-iridium. Strictly speaking the ore consists of two alloys, crude platinum containing all the six platinum metals, but with platinum predominating and osmium-iridium, also with all six platinum metals, but in different quantities. The crude platinum contains in addition to platinum, mainly palladium, rhodium and iridium, also smaller quantities of osmium and ruthenium. Osmium and ruthenium can be separated without much difficulty, as they can be converted by oxidation into volatile oxygen compounds, which can be removed by distillation. With ammonium chloride compounds of platinum and iridium are obtained, which are, however, difficult of solution, from which the metals are obtained by ignition. If the solution of crude platinum in aqua regia with ammonium chloride is omitted, then the precipitate contains besides platinum and iridium also, considerable quantities of rhodium and palladium and complicated methods have to be used to obtain the pure metal. On the other hand the platinum and iridium cannot be fully removed in this way and the mother

liquor of the ammonium chloride precipitation contains in consequence considerable palladium and rhodium, and also small quantities of iridium and platinum, and requires complicated working over. By means of the most exact analytical methods it has been ascertained that the purest platinum may contain a maximum of 0.01 per cent of impurities. Platinum sponge, that is the metal in a loose gray mass, is obtained by igniting ammonio-platinum chloride, from which the compact metal has to be obtained.

As platinum melts at the very high temperature of 17 to 1,800° Centigrade, there is a difficulty. At the commencement of the nineteenth century, the importance of platinum in the arts and sciences was recognized, but no means were available to obtain that temperature. The difficulty was first overcome by melting the platinum with arsenic into an easily fusible alloy, after which the arsenic was roasted out. More recently, the capacity of the metal for large welding was utilized. By means of high pressure the sponge was compressed, the cake formed was then ignited and hammered and thus the individual particles were welded together.

The great temperature required is now obtained with an oxy-hydrogen blow pipe, or in an electric oven. At present even higher temperatures can be reached. In the assay of platinum a platinum-silver button is obtained, which is parted by means of concentrated sulphuric acid. This process is wasteful as there is an appreciable loss of platinum, which may range from 20 to as much as 50 parts of platinum per thousand, as the boiling concentrated sulphuric acid dissolves some of the platinum. An improved method has been suggested as follows: About 250 mgrms. of the platinum alloy are mixed with silver (at least five times the quantity of platinum present) copper (a quantity equal to that of the platinum) and lead, cupelled at as high a temperature as possible and the residue fused for from 3 to 5 minutes. The resulting button is rolled to a thickness of 0.2 mm. and heated for a quarter of an hour with diluted sulphuric acid (100 vols. of concentrated acid to 22 vols. of water) at a temperature not exceeding 240° C. The acid treatment is gone through twice over and the residual platinum is washed, dried and weighed. Platinum also exists in ores of other varieties, thus in the Rambler mine, Wyoming, an ore is found consisting of sulphide and oxidized compounds of copper and also sperrylite containing platinum, $PtAs_2$. The richer grades of ore are hand sorted, but the greater portion of it is crushed and concentrated, both are dealt with by a smelter. The Rambler ores and concentrates are dealt with as follows: Eight portions of one assay, ton each, are fused with a suitable flux in 20 gm. crucibles. As in the Rambler ores there is a considerable quantity of copper, the resulting lead buttons are scorified until soft and are then cupelled. The buttons resulting from the cupellation are weighed to obtain the precise proportion of precious metal. They are then com-

bined in two check lots, representing four assay tons each and recupelled with ten times their weight of pure silver. The resulting buttons are then parted separately with a 12 per cent nitric acid and finally with concentrated nitric acid in test tubes placed in boiling water. Silver, palladium and platinum are thus dissolved and gold remains. The residue is then washed by decantation in the usual way, ignited and weighed; the nitric acid solution is kept as small in bulk as possible, after some further processes the filtrate obtained is made ammoniacal, then acidified with formic acid and boiled, platinum and palladium are then precipitated. No precipitate generally forms until after boiling begins and ebullition should be continued for half an hour, the precipitate is then filtered, washed and ignited and the weight gives the combined quantity of platinum and palladium, which are converted to chlorides by dissolving in aqua regia, evaporating to dryness and taken up with a few drops of hydrochloric acid and 50 cc. hot water. This solution is saturated with pure crystallized ammonium chloride; 10 cc. alcohol is added and the whole allowed to stand for not less than 24 hours. The precipitated ammonium plantinic chloride is then filtered, washed with a saturated solution of ammonium chloride and ignited very slowly on account of the possible volatilization of the precipitate. The resulting platinum is then weighed. Palladium is determined by the difference between the combined weight of platinum and palladium and the platinum precipitated by ammonium chloride. It may be interesting to compare the properties of platinum and gold, as the latter has on occasion been suggested as a possible substitute. The former is very resistant to the action of mineral acids, especially when cold, but in boiling concentrated sulphuric acid containing 90 per cent of monohydrate, platinum dissolves in the proportion of $14\frac{1}{2}$ grains to one ton of acid. The greater the concentration of the acid the more it will dissolve the platinum; the solubility of gold under such conditions is six times less. To the action of pure muriatic and nitric acids, platinum shows the same resistance as gold. In a mixture of muriatic and nitric acids the complete solution of platinum is reached by heating only, while gold is easily dissolved even cold. Water solutions of alkali produce no effect on either metal, but if strengthened with caustic alkali they act on platinum more than on gold under a red heat. Both in a pure state are relatively soft and tensile and can be stretched into very thin wire and rolled into thin sheets. The specific gravity of platinum is 21.1, and of gold 19.3; whilst the melting point of the former is $1,775^{\circ}$ C. and of the latter $1,075^{\circ}$ C. The electric conductivity of platinum is three times less than that of gold. So long as the value of platinum was less than that of gold it was used for many purposes, but when the value rose to a much higher level, efforts were made to find a substitute. In the chemical industry and laboratories platinum is occasionally re-

placed by other materials such as gold, silver, aluminum, porphyry, quartz, glass and so on. The manufacture of artificial teeth which had reached a high state of development in the United States, has absorbed large quantities of platinum. The teeth consist of a porphyry mass of a high melting point with a platinum pin. The high melting point and the coefficient of expansion (0.00088) are important points, but with the high price prevailing gold will be substituted. There are other purposes for which platinum is irreplaceable, such as contact substances for the delivery of acid, as applied in the manufacture of sulphuric acid, also for surgical instruments and thermocouples and instruments for designing on wood by means of burning. During the reign of Nicholas I of Russia, a platinum money was minted of 3, 6 and 12 rouble pieces.

Platinum only occurs in a very limited way in the United States, although it has been found in many localities, both in rocks and placers. There are platiniferous ores in Nevada, also in the Rambler mine, South Wyoming; in the former area they are found in the Key West group of mines in Buaherville. On the Pacific coast platinum has been found in placers in seven localities; one is Oroville, Cal., where it occurs in the proportion of 1 to 500 of gold. Other localities are Trinity county, Cal., and Josephine county, Ore., Surf, Santa Barbara county and San Luis Obispo, Trinidad Head, Humboldt county, Cal., Crescent City, Cal., and Cape Blanco, as well as the west coast of Washington are other localities. From the mouth of the Rogue river north to Coquille river the metal has been found. Platinum occurs in some of these localities in periodotite dikes of the custatite-mica-pricrite variety. Some horn blendite dikes also show upon analysis a trace of platinum. The foothills of the Virgin range at a height of 3,600 feet also disclose the metal. In some of these localities the ore cannot be worked as there are no railroads in the vicinity. Alteration and concentration of the sulphides in the rock by solution seems to increase the percentage of platinum.

After Russia the second largest source of platinum is the South American Republic, Colombia, where it is found mixed with gold, in the gravels of the Choco. The main source is the Platina and Condoto rivers, tributaries of the San Juan river. It is also obtained from some of the streams which flow into the Atrato river. Platinum was found in the Tulameen District, B. C., as far back as 1885, in placers. Gold and platinum were found in about equal proportions and are coarse with the rough, unworn surface characteristic of nuggets which have not traveled far from their original source. The platinum is sometimes associated with pyroxene, olivine or chromite. Platinum rarely occurs in large nuggets, the largest ever found in the Russian Ural district weighed 252 ozs., Troy. In the Tulameen district half an ounce is probably the maximum, it is usually in small pellets, rounded.

GAS CAVITIES, SHOT, AND CHILLED METAL IN IRON CASTINGS.*

About eight months ago, at the request of the writer, the foundry journals and iron trade papers of this country and Europe kindly published an article soliciting samples of iron castings showing globules in gas cavities, solidly encased shot iron, hard streaks or spots in castings, and white areas inside of gray or soft iron. Those good enough to forward such samples were requested to give the following information:

1. The character of pig, scrap, fuel and any flux used in melting the mixtures; also if anything unusual occurred or was observed during the heat; grade of the iron produced, whether soft, medium or hard, or better still an analysis of the casting and the defects, whether shot or white iron.

2. A rough sketch of the casting showing its shape, and the thickness of the different sections as far as possible, marking the location of the defects on samples forwarded.

3. Whether the mold was of green sand, skin-dried, dry sand, or loam, and a description of gating and pouring.

4. Whether the metal at the time of being tapped, as well as being poured into the mold was "hot," medium, or "dull," and any other information that might be thought of value in assisting an intelligent research of the subject.

Losses by defects as stated in the subject title above have caused many firms much worry and trouble before they could be made to disappear. The greatest annoyance, however, would arise from the fact that the trouble would be abated, but its origin could not be traced, and hence intelligently guarded against thereafter. As one of the letters received by the writer from a prominent Massachusetts firm is very pertinent, an extract from it is given herewith:

We note that you are accepting samples and suggestions regarding the formation of hard shot in cast iron and think perhaps some of our experiments will be of interest to you. From time to time we have had trouble with this shot forming in castings which we have made. A great deal of this work is finished, and as shot in it is always sure to knock out the forming tools, so that they have to be reground, we have tried almost everything to stop this, and even when it does stop we do not know what we have done to do it.

We conceived the idea of trying to make this shot in the iron, thinking that perhaps if we found out how to make it we could see how to stop the trouble. Our chemist informed us that the "shot" was caused by the foundry "mesh bugs" or small particles of chilled iron that drop in the meshes in the foundry. These, he stated, trickled down through the charges and were not properly melted and run into the molten metal, in this way forming the shot.

We took some of these bugs and put them into the ladle and poured castings from them, but were unable to make any shot. We also tried hard rattling stars, small set screws and small pieces of steel and were unable to produce any shot. We tried putting these hard materials in the mold and pour-

ing the iron in the mold on top of them, but with the same result—no shot. We then wet a gate in the mold in an attempt to make the mold blow, without results. Damp, wet sand, while it caused blow-holes, did not produce the hard shot.

In fact, we have tried everything that has been suggested that might cause this trouble, trying to make the hard shot, making the test as favorable to the formation of them as possible, and have been unable to produce anything. We are therefore coming to the conclusion that there must be something in the mixtures of iron and are going in on that basis to try to cure it, although at the present time we have not had any trouble. We have no samples to send you, but should any come along that show this formation, we will forward them to you.

Another experience along the line of the above firm is given by a large concern in New Jersey, in the following extract, taken from a lengthy letter giving experiences, mixtures, etc.:

The castings were nice and soft, and the only trouble, which, however, was serious, was with the small, hard shot. At one time we were using hard iron stars for cleaning, and some of these stars got mixed up with the sprues and scrap, and we thought the hard spots were caused in this way. However, when we eliminated all possibility of a mixture having hard iron stars we still had the trouble with the hard spots in the castings.

The above two experiences, with others that might be given in addition, would suffice to counteract the

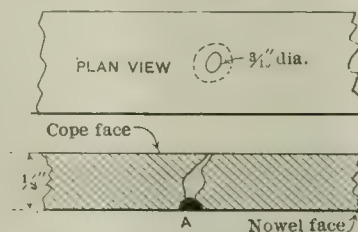


Fig. 1.

theory often advanced that small chilled or hard bodies going into the cupola may cause hard shot, streaks, or spots in the iron castings.

A few weeks after receiving the Massachusetts letter, this firm sent a sample of defective casting showing a small, hard button or "shot" loosely embedded within the nowel or down cast face of its surface. The sample (see Fig. 1) shows a crease made when the tool swerved off to one side in striking the hard spot. Also the chiseled indentations caused by removing the hard shot or button from the planed face of the casting. This defective sample is about as interesting a one as any received by the writer.

The peculiarity of this sample lies in there being a vertical, small blow-hole leading directly from the top of the hard shot seen at A to the cope surface, so that upon removing the shot one could see clear through the body of the casting, this being about a half inch thick. It gives evidence of the hard shot or foreign material while lying near the bottom surface of the casting emitting a gas which went upward through the molten metal to the sand surface of the cope, but not sufficiently fast to prevent the creation of the small, vertical blow-hole shown. In order to clearly observe the full surface and character of this blow-hole the sample was fractured and the hole is sketched closely, as

*From Castings.

seen in Fig. 1. It is rather unfortunate that samples showing hard shot, etc. (A, Fig. 1), are so small that they do not afford sufficient material for making a complete analysis, as this would no doubt assist in the solving of such problems.

Several samples of soft iron castings have been received containing solidly encased or cemented small bodies of strictly white iron. The term "cemented" is used here, as the spots, or white bodies, are in nowise loose in the castings. They form a part of it, showing differences in color of white and gray, but are as solidly united as this is possible for any two plastic materials, each of a different grade and color, to be so. Not only is this defect obtained in a shot or spot form by founders, but also in streaks and bodies of considerable area. Defects of these characteristics are most generally found at the upper cast body, face or edge of castings.

Some shot iron was received by the writer which had been taken from a cupola spout after the bottom was dropped, on the supposition that it could cause blow-holes. Some of this shot he placed in the bottom of an "open sand" mold giving small castings, about three-eighths inch thick. In pouring these, no disturbance of the metal through any escape of gases was noticeable, and when the castings were broken through sections containing the shot they were perfectly sound. The writer also used some of the shot by placing it on the bottom of closed molds, and pouring some of the molds with "hot" and also with "dull" iron. In one case of "dull" iron, a very small gas cavity or blow-hole was barely noticeable above the top of the shot. The party forwarding the shot stated none were observable at the first of the heat when nearly all pig iron was being melted, but noticed them at the latter part of the heat when the charges were composed largely of scrap iron.

The above shots were sufficiently soft to be squeezed or flattened slightly before cracking by placing them between the jaws of a vise and applying pressure. The experiments conducted by the writer showed, aside from the "blow" question, that unless shot iron was up to a very high red heat, or near the fusing point (as is possible in many cases when they are formed in pouring a mold), that casting metal under three-eighths inch in thickness would have little effect in melting them, unless they might rise to be embodied in nearly the middle body of the casting, especially if the shot are roughly over one-eighth inch in diameter. The shot which the writer used in the above experiments were placed on the bottom face of the mold at the end farthest from the pouring gate, so that the wash of the metal would not be so liable to disturb them. An examination of the castings when cold showed the shot in their original position and not united to the body of the castings, when fractured along a line in their position.

The logical reasoning regarding the creation of the small, hard particles or metal shot found in some cast-

ings, is that they become suddenly separated from the general mass of metal during the pouring of a mold. When thus separated they solidify so quickly that not sufficient time is given for the carbon to be separated out as graphite. Hence the shot does not have the softness of the rest of the casting which had more time to cool.

The longer the distance a shot is sent through the air before it lodges and the cooler the air it passes through the harder the shot. Affecting this also is the degree of dampness of the spot upon which the shot may lodge. Where shot is caught and covered by incoming metal before it has time to become cooled below

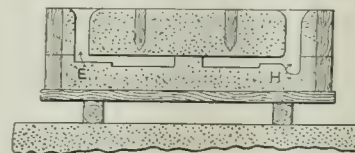


Fig. 2.

a red heat, the chances for their being hard and discoverable in a casting is not of course nearly as great as when they can become of a dark color before being encased by the liquid metal.

Particles of iron or shot may be formed during the falling of the metal from the ladle's pouring lip by striking the sides of a pouring basin or gate; or, by falling upon a flat bottom inlet gate, as at E, Fig. 2; or when the metal reaching the mold strikes some obstruction fronting the gates to splatter the metal. In ordinary plain work there is probably no feature so harmful in causing a splattering as having flat gate bottoms, as at E. The bottom of all pouring gates should have



Fig. 3.

more or less of a well, as at H, Fig. 2, as by this formation, if there is hesitation for a moment or so when starting to pour, the first droppings from the ladle fall into the well shown, to stay there in a liquid bulk and not be splattered to create shot.

In starting to pour the majority of molds, especially those of a light work and stove-plate character, there should be no momentary stoppage after starting, but from the instant the falling metal first strikes the bottom of a gate, as at H, there should be a steady and unbroken stream to rapidly fill the pouring gate and have it kept so until the mold is filled. This applies to the flat top pouring gates generally used for stove-plates, etc., as well as those of the joint character, shown in Fig. 2. Following of the above practice closely in all admissible cases should help greatly to end

some of the trouble experienced with shot iron and hard spots in castings, and is one illustration of where the master's skill in handling a ladle can be displayed.

The too free use of a swab or sponge in wetting the joint of a mold, before drawing a pattern, or after this is done in finishing a mold, can easily harden or chill the metal parts of a casting formed where this excessive dampness existed. Again, also, by too damp a mixture of sand, hard ramming or insufficient venting. Metal striking these damp sections will often bubble and splatter to a greater or less degree. This action can in some cases create suddenly chilled shot that will be carried to other sections of a mold to become encased in liquid metal and thereby give the white iron or chilled shot found in some castings.

The above is not intended to account for all the white iron, chilled shot, streaks, etc., found in castings, especially those of a light work and stove-plate character. However, a solution of the phenomenon seen in

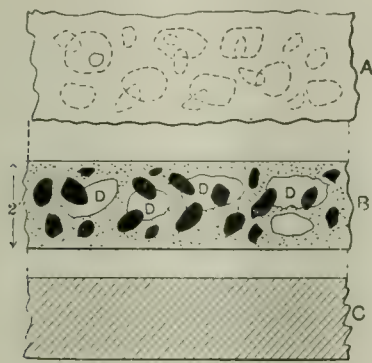


Fig. 4.

Figs. 5 and 6 relating to "inside chill" should greatly help foundrymen to prevent some of these annoying and costly experiences.

As white iron or hard spots can be produced at will in gray iron castings, especially those of a light character, by the immoderate use of the swab or sponge, damp sand, hard ramming and insufficient venting, this would indicate that the skillful, broadly experienced overseer and molder can master many troubles along these lines.

While we have both the melting and molding end of a foundry to watch in order to discover many of the troubles cited herein, it is to be said that the lack of a capable overseer, as well as of well-trained molders, is often responsible for their creation.

There should be no division of responsibility. The head foreman or superintendent should be a master of mixing and melting, as well as of molding. The opportunity for shifting this from one to the other may easily cause the overcoming of these evils as well as others to be a very difficult task, the proprietors or stockholders paying the losses while contention lasts.

The next defect to be taken up is that of globules in gas cavities and blow-holes, an illustration of which is seen in Fig. 3. These defects can be due to two conditions but emanating from one cause, and that is the

creation of excessive gases or steam that cannot find its liberation from imprisonment within a body of solidifying metal. They are found chiefly in the upper body or cast end of castings.

Excessive gas, causing blow-holes or cavities, may

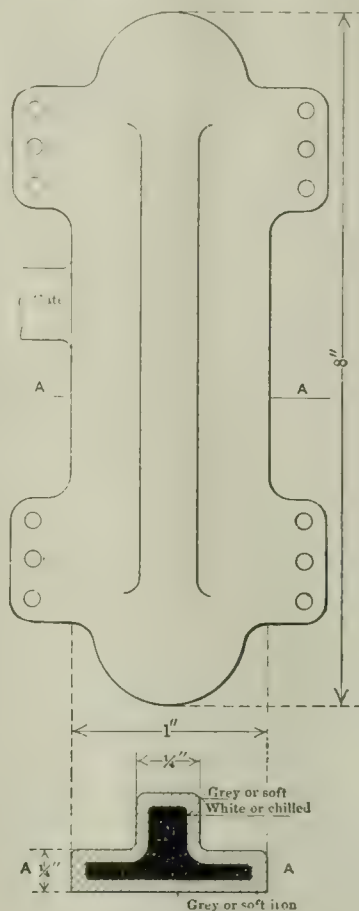


Fig. 5.

come directly from the metal or wholly from defects in molding or pouring. Those due to the iron may be caused by oxides of iron or manganese reacting on the

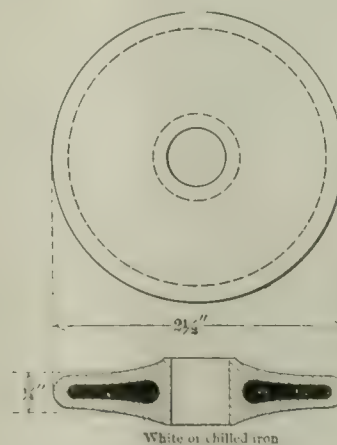


Fig. 6.

iron's carbon, the former producing carbon monoxide gas, or on liberated graphite creating kish (although of the latter there is very little in remelted iron, it being chiefly found in direct metal at blast furnaces). Also indirectly through sulphur, by reason of the form-

ation of sulphide of manganese. And again by a foreign body like that possibly created by the mixture of iron oxide and dross (the latter may contain some kish in connection with the dirt generally coming from clays of the cupola tap hole and spout, and other sources) forming a slag on the top of a ladle's metal that could pass in small bodies into a mold at the starting of pouring, or later on before a mold is filled, through defective skimming. Thereby often large as well as small blow-holes or gas cavities are formed. As a side issue it can be said that a ladle's surface dross can easily cause dirt-holes, pin-holes, and a dirty surface to the finish parts as well as the rough surface of castings when skimming is at fault in pouring a casting.

Gas cavities and blow-holes due directly to defects in molding and pouring are often due to not having properly tempered sand, regulated degrees of hardness in ramming, efficient means of venting, and correct methods of finishing cores and molds, combined with needed experience in gating and pouring. These are all factors demanding the experience of a decade or more in the actual work of general molding, in order one may be fairly qualified to best prevent the occurrence of the difficulties treated herein, or to stop them quickly when in evidence. The truth of all this is demonstrated by the difference in the soundness or perfection produced in castings by the master molder and the one that is not.

It may be asked whether molding machines would not assist in preventing some of the above defects. Molding machines, owing to the following of an exact routine, adopted after much experimenting as the best to insure desired results, cannot but be helpful to a large degree in removing the liability of steam and gas cavities, or blow-holes, chargeable to molding. This is not saying that they will remove the liability for all the defects treated herein, or that there is no demand for the master molder or the research and knowledge such a paper as this imparts, as these can and will be greatly utilized as long as there is a demand for castings or the need for melting iron.

Globules when suspended from the roof of a cavity, as at B, Fig. 3, are evidence that the cavity is probably due to something being wrong in the method or manner of making, gating or pouring the mold then directly with the metal. The mold's gases or steam creating these cavities may be originated during the filling of the mold, and again may not until sometime after the mold has been filled, or before the main bulk of its metal solidified. Imprisoned gases or steam, due to defects in molding, form a cavity into which the outer body of liquid metal may with favorable conditions ooze to form loose shot or suspended globules, as seen at B, Fig. 3. The actions of globules or any liquid, also any special elements, finding access to such cavities may continue at intervals for a short time after a gas cavity has been formed, or as long as the body of metal surrounding the cavity remains in a fairly liquid state.

The larger the cavity the greater the chances for this action. Globules finding access to a gas cavity at its upper end, as displayed in Fig. 3, may be credited to the law of specific gravity and also to the condition that heat rises and that the upper body of metal is as a rule more fluid than the lower, as is evidenced by the "hot spot" or shrink hole being the greatest in the uppermost cast end of castings.

Cavities created solely through conditions of the metal, or its constituents, or again strictly by splashes of oxidized bodies of metal, or foreign solid matter, should by logical reasoning more generally present an unbroken smooth bright surface. The metal, or confined oxidized shot conditions that start these cavities are such as can in some cases continue the creation of gases to make a higher internal pressure to prevent globules, liquid metal, etc., entering their space than exist where gases become imprisoned from a source that cannot add to their volume, or increase their pressure, as would more generally be the case if created wholly by defective molding.

A casting may possess gas cavities that will be due to causes inherent in both the mold and the metal. This for one case, as an example, could occur through a mold bubbling or boiling its metal sufficiently to throw up small bodies or buttons of metal that would fall back oxidized into rising metal in the mold, and these bodies, buttons or shot could, by reason of their oxidization and probable gathering of dross, create a gas to cause cavities that would be companions to those created solely by the mold's steam or confined gases endeavoring to escape, but was imprisoned in the metal. See Fig. 4.

It is possible that sulphur or phosphorus may create blow-holes, or the globuled roof perforated gas cavity, but with my experience of forty-eight years as an active molder and shop manager, making all kinds of castings in green-sand, dry-sand and loam work, knowing something thereby how castings can and should be made, I have little faith in the common "chestnut" excuses of sulphur or phosphorus forming blow-holes in gray iron castings.

In thinking back over my long years of experience I cannot remember ever having seen a blow-hole or gas cavity in a strictly gray iron casting that I could believe came from any other cause than defects in molding. With castings that have come under my own making or supervision having blow-holes or gas cavities, I always proved this faith by the discovery of defects in their molding, etc., and making changes in the work that would stop them.

Where mixtures are of a hard or chilling iron I stand ready to more seriously consider the sulphur and phosphorus excuses for blow-holes or gas cavities, etc., in castings, but for soft or gray irons I desire to maintain the above position until it is positively proven I may be in error.

Among the letters that have come to my hands for consideration of this subject is one from P. Munnoch

of the British Foundrymen's Association, as it presents some excellent information obtained by hard research work I take much pleasure in presenting the same in the following twelve paragraphs and three tables of analysis:

TABLE I.—ANALYSIS OF "METAL, SHOT AND BUTTONS" FROM CASTINGS.

	1	2	3	4	5	6	7	8	9	10
Fracture.	White.	White.	Mottled.	Mottled.	Mottled.	Mottled.	Mottled.	Gray.	Gray.	Gray.
Graphite carbon . . .	.33	1.16	..	..	1.68	2.02	2.44	..	2.45	
Combined carbon . . .	2.20	2.00	1.25	1.00	..	1.05	.75	.76	..	.85
Silicon . . .	.70	.84	.93	.60	.86	.93	.98	1.26	1.14	1.32
Manganese . . .	.63	.59	.48	.63	..	.36	.50	.45	..	.43
Phosphorus . . .	5.68	5.45	4.88	4.84	4.64	3.80	3.20	1.92	1.80	1.70
Sulphur . . .	.016	.031	..	..	..	.021	.037	.046	..	.031

Taken from casting

TABLE II.—ANALYSIS OF CASTINGS FROM WHICH SHOT WERE TAKEN.

	A	B	C	D	E	F
Graphite carbon.....	2.74	2.80	2.90	3.25	2.80	2.85
Combined carbon.....	.62	.50	.40	.05	.60	.60
Silicon	1.63	1.72	1.70	1.77	1.95	1.65
Manganese	.51	.49	.45	.44	.48	.49
Phosphorus	.88	.83	.89	1.23	.95	.84
Sulphur	.091	.118	.114	.107	.105	.119

All the above analyses were cylinder heads except E, which was a pedestal.

The chief peculiarity noticed in connection with shot is that they usually occur in the upper portion or near the upper surface of a casting. Generally they are small in size and almost round. In some cases they entirely fill the cavity in which they are formed, in others they only partially fill the cavity.

When fractured the appearance varies from gray to white. When machining castings the tool will usually jump over the white variety, as this is extremely hard.

The analysis given in Table I shows the composition of shot and buttons and also composition of castings from which these were taken. They are arranged according to phosphorus content. Several of these analyses were mentioned in a paper entitled "The Practical Application of Chemistry in the Foundry," read before the British Foundrymen's Association, August, 1908, by the writer. They were also mentioned in a paper on "Iron Sulphur and Phosphorus," by J. E. Stead, at the same meeting.

Most of these analyses are from specimens obtained from large castings. In some cases several ounces in weight were obtained, the holes from which they were taken being very much larger than the buttons of metal found in them.

My first experience was with gray shot inclosed in small castings. The small sizes of these shot yielded metal for partial analysis only and did not reveal anything to any great extent different to the analysis of the casting from which they were obtained. In some cases these were apparently shot of metal splashed into the mold at the commencement of pouring, and then after oxidizing on the surface became inclosed in the liquid metal. Afterwards I came across some peculiar castings from which I obtained large buttons and pieces sufficient to make complete analysis from. The analysis showed that these could not be merely splashes of the original metal, but must have been liquated from the interior of the casting after the greater part of the metal had solidified. The analysis of the buttons appeared very similar to that of the metal drops

squeezed out of phosphoric pig iron after the metal had solidified, by submitting it to hydraulic pressure, in some early experiments by J. E. Stead, F. R. S. I therefore submitted some of the specimens and analysis to Mr. Stead, and his opinion was that blow-holes were first formed, and these afterwards became filled with the highly phosphoric liquate. I examined castings from various sources and found all more or less troubled with this defect. I obtained many specimens, in some cases sufficient for complete analysis, in others hardly sufficient for a single determination.

Some large cylinder heads for blowing engines supplied many interesting specimens, pieces several ounces in weight being obtained. See Table II. In some cases pieces or buttons of different compositions were obtained from different parts of the same casting and pieces of different compositions were found in the same cavity. The castings weighed about ten tons, the thickness varied considerably and the molds were largely built up of cores, some of which were difficult to vent satisfactorily. The castings were square, with a circular web and flange running around the top, and the holes were formed in the top flange. The holes were only revealed after machining and after removing a good thickness of metal. The holes were large and the interior in most cases was bright, but in one or two cases small masses of oxide were found. The upper surface was smooth with rounded projecting crystals, indicating the rising of gases after a considerable thickness of metal at the top of the mold had set. The lower part of the cavities showed signs of shrinkage in places, but the bottom was usually covered by the liquated masses.

The buttons themselves were smooth, with a bright, mirror-like surface, which they retained after several years' exposure to the acid fumes of the laboratory. The buttons were rounded at the edges and therefore could not have been very fluid when run. In some cases small shot were partly inclosed by larger masses, and this, together with the difference in composition, showed that the liquated metal had not all entered the cavity at the same time, but at different periods of solidification. In some cases the small shot present appeared to have been squeezed into the cavity. The gray shot were similar to the casting in fracture, the mottled shot not unlike ordinary mottled iron, the white was much like white iron, but the outside part showed a crystalline appearance in the form of long crystals interlaced and partly covered with a thin layer of graphite in some cases.

There was evidently a contraction of the outer shell or expansion in the interior set up after the metal was almost solidified and the pressure set up caused the still liquid portion to be squeezed from between interstices of the already formed crystals into the cavity formed previously.

For comparison, analysis of liquid which is squeezed out of low phosphorus forge pig iron is given in Table III. In this case the exterior is solid and the contraction of the shell or expansion in the interior forces out some of the still liquid metal from the interior. In the case of the castings it is not the still liquid metal which is forced into the cavities, but the phosphorus enriched liquid remaining in the spaces between the crystals, at the time when the pressure is set up. The liquid is gradually enriched in phosphorus until the phosphide eutectic containing 6.7 per cent phosphorus, 2 per cent carbon and 91.3 per cent iron is reached, and the amount of phosphorus in these buttons is an indication of the period during solidification at which they were formed. The shot in which the phosphorus is very little different to that of the castings may in some cases be due to splashes of metal entering the mold at the commencement of pouring, becoming coated with oxide and becoming simply encased in the following molten metal. Or shot may be formed by a compressive action similar to that illustrated in the case of forged pig iron, in which a portion of the still liquid metal in the interior of the casting is squeezed into a previously formed hole. In this case composition would be much the same as that of the casting in

which it is found. This is an example of shot that might be formed in the outer solidified part of a casting the interior of which is still liquid. In the case of high phosphorus shot, the lique enters the hole after the casting has practically assumed the solid state. The last portion of a casting to become solid, the interior for example, is not found to contain more phosphorus than the outside parts of the same castings, in fact in spongy parts of a casting the opposite is sometimes the case, as the phosphorus enriched liquid between the crystals has to some extent been drained away.

Generally the formation of shot holes and shot are most noted in iron which has been subjected to oxidizing conditions during melting. Instances of this may be seen when the first metal from the cupola runs cold, particularly when the softer varieties of iron is being melted. If this is caught in a ladle and allowed to solidify it often presents the appearance of a spongy mass full of shot, the holes and shot being coated with oxide and graphite. Should some of this be left in the bottom of the ladle and some hot fluid poured over it, a boiling action follows, and if poured into molds the castings produced contain many holes of the shot hole type. Holes of this kind may be bright or tinted inside; they usually contain specks or flakes of graphite and often contain particles of oxide in the lower part.

At blast furnaces where low phosphorus pig iron is produced it is noticed that after the iron is run into the pig molds and the metal appears to be solidified on the outside, the still liquid portion in the center squirts out and forms small mounds near the sow end of the pig. This is no doubt due to compression of the liquid in the interior due to contraction of the outer solidified portion. This phenomenon is only noticed in the forge variety of pig. It is also often noticed that the holes in the upper part of the pig often contain shot and buttons of metal and in low phosphorus pig iron these are usually similar in analysis to the pig iron itself.

The above description, analysis, etc., of Mr. Munnoch's researches are exceedingly valuable. The writer offers the following comments on causes and remedies for the defects cited. The first item he would call attention to is Mr. Munnoch's statement of "some castings weighing about ten tons, with thicknesses varying considerably, and the molds were largely built up of cores, some of which were difficult to vent satisfactorily." If I were asked what was the cause of the buttons, shot, gas cavities or blow-holes in the castings cited by Mr. Munnoch I would, to make a brief reply, say: *the molds*.

TABLE III FORGE PIG IRON (LOW IN PHOSPHORUS) WITH PORTION SQUEEZED OUT.

	Pig iron, Per cent.	Liquate, Per cent.
Graphite carbon.....	3.06	3.30
Combined carbon.....	.78	.58
Silicon.....	1.23	1.30
Manganese	.78	.82
Phosphorus	.043	.046
Sulphur	.091	.034

The character of the metal used had practically nothing to do with their creation. In other words, could the molds forming these castings have been poured with right temperature metal, through well-constructed skinning gates, without the occurrence of a flurry, bubble or boil, as the mold was filling up, or afterwards in the metal solidifying and being brought to a solid state by proper feeding, I venture to say that all the castings he cites could have been cut up into 1-inch cubes and not a single gas cavity or button of metal

would have been found in any one of the thousands of cubes that would have thus been formed.

Mr. Munnoch shows that he obtained some very large specimens of shot or buttons, such as a bubbling or blowing mold could easily create. To obtain some practical ideas on this point requires one to watch the action of but a few blowing molds. A bad blowing mold can often throw much of its metal three or more feet high, if risers and feeding heads were blown or left open to allow the boiling metal free play to kick and jump as the explosive force of encased steam and gases would compel it to do. Metal blown up must come down. In doing the latter it is easy to discern how very large globules or buttons can be formed by small bodies of metal lodging on flat planes, projecting bodies, flanges, etc., of a mold. Or again to fall back directly into thick or thin baths of dull rising metal. These buttons or shot having been oxidized or covered more or less with a dross collectible in their upperward and downward flight, would naturally create some gas cavities when liquid metal surrounds them.

Another point that should not be lost sight of is the great chances there are for the creation of blow-holes entirely free of either buttons or shot in castings in which the metal had bubbled or "blowed" when they were being poured and cooled to a solid state.

A close study of the gas cavities cited by Mr. Munnoch shows that there were two kinds. Some of these were formed by the gas created from an embedded button or shot. Others by the sole effect of gases or steam created by a mold or its cores endeavoring to escape from imprisonment, but being caught formed cavities into which were forced particles of the surrounding metal to form buttons, or shot that might hang to their roofs, or be loose in the cavities. A perplexing part of Mr. Munnoch's discovery lies in the difference of the chemical constituents of two buttons that he cites as having been found in the same cavity. There is much embodied in Mr. Munnoch's commendable researches that will no doubt incite further study and investigation contingent to this subject, aside from what can be charged to the direct responsibility of the molder and his overseer.

The writer's receipt of letters and samples brought some replies that while not strictly in the line sought for, bordered upon them so closely they are valuable enough to be considered herewith. One special case having a very close bearing on others of a similar character is that of a foundry foreman in California having a large retort casting rejected on account of the existence of many cavities and large buttons of metal mixed with masses of dross in a certain location of the cope section of his casting. The sample forwarded is seen at Fig. 4.

Upon corresponding for particulars I came to the conclusion that the defects were wholly due to the method of gating used. The mold was of green sand and the metal rushing into it cut against some green

sand fronting the gate for fully thirty seconds or more before it reached a level of the gate, so as to have metal in front of it to retard its cutting action. The inflow of the metal at the gate would on directly striking the bare face of the mold splatter in all four directions. The separate particles would fall back in partly solidified small bodies to often lodge on the top of the dross created by the cutting action of the mold's inlet gate. As the metal rose slowly in the mold it lifted the accumulated bodies of mixed dross and solidified buttons of metal carrying it all upward until striking a horizontal plane that imprisoned it to await a complete filling of the mold and solidification of the metal in it.

An experienced molder and foundry superintendent in writing from New York State says:

The writer cannot furnish any specimens just at present, but I had a little experience at one time that always comes in mind very vividly and causes me to sit up and take notice when any one talks "shot iron" or "blow-holes."

A few days after taking charge of a new foundry in this state I was introduced by a mutual friend to a machine shop proprietor as a man who would cause all his troubles to end with castings as soon as I commenced to make them for him. I at once received an order for ten sets of milling machines, the V slides of which required to be perfectly free of blow-holes, and clean when finished. The castings were made and were all cleaned up to look A No. 1.

In about ten days after their delivery a drayman hunted me up to say he had a big load of defective castings. I found the same to be the ten nice milling machine beds I had made for the man to whom I had been introduced as a person who would put an end to his receiving bad castings. Every one of the castings had been on the planer, and all showed "shot iron" in the top and cope V's. It was the biggest bunch of bad castings I ever got back at one time or since.

I had been handling this particular job quite a distance from the cupola, and had to change the ladle from one crane to another in order to pour the molds. Before starting to replace the bad castings I figured out that the shot was formed by the air in the mold, and while the metal was traveling over the body of the cores also that the shots were carried up into the top V's and the metal was not "hot" enough to remelt the shot. I put the job where I could swing a ladle right from the cupola to quickly pour the castings, and never lost another one because of "shot iron" in them.

The contention of the writer herein for molds being more responsible as a general thing than the iron for the creation of blow-holes, etc., is not to be taken as meaning that there is nothing to be feared by gases that may emanate directly from some irons. We have, of course, as is shown by Mr. Munnoch's recital of oxidizing conditions during melting, an evil that is to be combated, but the writer contends that this is a feature for which the overseer or shop manager is often largely responsible and can as readily be guarded against as can evils in molding. A metal that is dangerously loaded with an oxide of iron is readily observable to the practiced eye of an experienced foreman or shop manager, and only the roughest of castings should be poured with it, if such metal has to be used.

Light work suffers, as a rule, from the oxidizing conditions of melting and handling metal more than

heavy work, causing light work foundries to often have much trouble with hard spots, hard streaks and pin-holes in their castings, shot iron in gas cavities being little in evidence with them.

The action of oxides of iron in liquid metal is a good deal like that of excessive sulphur; it reduces fluidity, causing metal to be sluggish and scummy. Melting iron "dull" oxidizes it more than melting it "hot." The higher temperature protects the metal better from being oxidized by reason of its dropping more quickly from the cupola's melting point through the fuel to its bottom bath and also by reason of the manganese and silicon in a mixture being brought to a higher fluidity to thereby the better assist the creation of a fluid slag for floating over a metal surface in a cupola's bottom to the more annul the direct oxidizing effect of the blast.

Anyone giving much study to the various defects treated by this paper cannot but be greatly impressed with the importance of melting iron so it will come down as "hot" and fluid as practical, as an agent to help prevent many of the defects cited herein. It is to be remembered that if metal is too "hot" to pour a mold it is much easier to cool it than to make any endeavor to increase its fluidity by reason of adding alloys or compounds to metal when in its ladle.

Quite a large number of alloys are now manufactured for the purpose of eliminating the natural and acquired impurities in iron, some of which may cause the defects treated in this paper, especially for light work. A large portion of these alloys are composed chiefly of manganese, and with the exception of where they are intended to strengthen iron, or give it some peculiar character, they can achieve little or no more than manganese used solely by itself.

We also have aside from manganese as currently known, silicon and phosphorus, all of which are obtainable in a ferro form with other constituents. The manganese ferro being as high as 80 per cent, the silicon 50 per cent and the phosphorus 20 per cent, and each obtainable in a lump, pea or ground form. These ferros are best used by being placed on the bottom of a ladle and having the metal tapped onto it, to be sometimes assisted in their work by the metal being agitated with a green stick or rod of iron. The amount of these ferros to be used will depend on the character of pig and scrap melted in connection with that required in the casting. The three ferros can be used from having $\frac{1}{4}$ pound to 1 pound of either per hundredweight of metal in the ladle.

The phosphorus serves as a scavenger when used to purify metal, by reason of its increasing the fluidity of the metal to thereby permit sulphur, oxides or occluded gases a better chance to escape. In connection with the above we have aluminum that can be placed on the bottom of a ladle to the extent of $\frac{1}{4}$ pound to 1 pound per hundredweight of metal in it. Aluminum is obtained from being all pure down to 85 per cent of it in alloy with other constituents. Fer-

romanganese and silicon are also used in the cupola along with lime or other fluxes to help deoxidize and desulphurize mixtures of iron. The above current generally known points of this paragraph are given here to make this paper more complete.

We have now come to a phenomenon that exceeds most any that might be mentioned in foundry practice, for being of a character that so far has not been satisfactorily explained, at least not to the writer's knowledge. The solution is one that presents conditions that are evidently as unreasonable to exist and be explained, as if one would in hitching a horse to a wagon find the wagon pulling the horse and then endeavor to demonstrate the cause.

The occurrence of "inside chill," so called by Mr. Walter H. Wiard, chemist of a large foundry firm in Illinois, who wrote me on this subject, is so seldom as to be never seen in a life's experience of a great many foundrymen. Nevertheless it is important that we should know the cause of this defect if such information can be obtained. An extract of the long letter sent me by Mr. Wiard states:

As I have met with an excellent example of this peculiarity of cast iron, I take pleasure in submitting to you all of the data I have at hand.

This phenomenon has occurred only once in the last nine months to my knowledge, and I am told it is the second time it has happened within the last two years.

Only two kinds of castings were complained of out of a probable heat of eighteen tons of castings of a similar nature.

I am inclosing a rough sketch of the castings. The inside chill extended throughout the entire casting and the demarcation from the soft iron was very sharp and distinct.

Following the above, Mr. Wiard's letter gives a very complete description of iron mixtures and methods of melting, etc., but believing this can offer no basis to account for this unreasonable phenomenon shown by Figs. 5 and 6, made from sketches forwarded to me, I have thought it best not to take space to print the same.

Explanation for the "inside chill" has been published, but as far as I can remember did not receive my approval and led me to believe that some experimenting to actually produce such results at will were necessary before anyone could feel satisfied with a solution of this problem. This the writer hopes to take up in the near future, as an aid to this end he kindly solicits the experience and views of any that might think they could throw any light on this subject, as well as any of the other points treated by this paper.

The value of the brick, tile, fireproofing, pottery, and various other clay products made in Iowa in 1911, according to the United States Geological Survey, was \$4,432,874. This is a considerable decrease compared with the figures for 1910.

According to the report of the Minister of Mines, British Columbia has produced 34,622,133 tons of coal since the inception of the industry in 1836.

BRIQUETTING OF CAST-IRON CHIPS.

In a recent issue of *Stahl und Eisen* Mr. A. Meseschmidt describes several new processes of briquetting iron and metal chips. The following translation of this article has been taken from the July *Castings*:

New processes of briquetting iron and metal chips are those of Weiss and Ronay, which consist in the main in pressing chips together under great pressure; the former employing a binding material, the latter using none.

In treating the question whether chip briquettes are useful economically, can be made to supplant the cast-iron scrap, and on the physical side can give good castings, the following questions must be answered:

Does the briquette disintegrate into its component parts through the effect of the heat?

Does the disintegration take place in the melting zone as in solid charges or above same where charged iron begins to get red and takes its first amount of sulphur from coke?

One must remember that probably the iron does not melt gradually but suddenly as soon as chemical combining forces have been destroyed by a certain tem-

TABLE A.—BRIQUETTES USED IN CASTING.

	Machinery castings.		Cylinder castings.	
	Number briquettes.	34 per cent cast iron briquettes.	Number briquettes.	35 per cent steel and cast iron briquettes.
Waste in per cent.....	4 to 5	4 to 5	4 to 5	4 to 5
Tensile strength, pounds per square inch.....	24,100	27,400	29,800	40,700
Price per ton of charge....	\$1.82	\$1.86	\$1.94	\$1.86
Price per ton steel briquettes		2.00		2.00
Price per ton cast-iron briquettes		2.12		2.12

perature. In case of briquettes it is very probable that the briquettes disintegrate far above the melting zone of furnace as their component parts are not combined chemically but only mechanically. Cast-iron chips lose much of their free carbon far above the melting zone of furnace. With a 30 to 40 per cent charge, the iron will be low in carbon and give a casting of great density but small tenacity. Another circumstance is the marked increase of sulphur and some phosphorus.

If briquettes disintegrate above the melting zone, the path which the liquefied and red hot iron particles take in the furnace is longer than the path taken by solid charges. There is greater oxidation of silicon and manganese and greater waste, as also increased percentage of sulphur, and in some cases of phosphorus. Of course the bad influence of sulphur can be met by adding silicon 2 per cent with about 0.12 per cent sulphur or 1.1 per cent silicon with 0.08 per

cent sulphur. To do this, briquettes can be mixed with iron and steel chips which will work against the sulphur influence. As for the phosphorus percentage, which is not large, it is often beneficial, as it tends to decrease the bad influence of sulphur.

The two systems of briquettes already mentioned, pressed together at pressure of 28,400 lbs. per square inch, differ only in that Weiss uses milk of lime and water of lime as a binding medium, while Ronay uses no binding medium at all. The form of these briquettes is cylindrical, about 5.6 in. in diameter and 4 in. high, with both ends slanting.

The specific gravity varies between 5.0 and 5.8, which makes them almost equivalent to solid charging matter. Tests with briquettes made by the old system proved unsuccessful in every respect.

A comparison of Ronay's with Weiss's briquettes showed that the milk of lime decreased waste from 3.39 to 2.76 per cent, a decrease of 0.63 per cent, which is not great but still worthy of consideration.

The Borsig Works, Tegel, Germany, have made extensive tests with the briquetting method in cupolas and found the following results, shown in Table I. Increased resistance to tensile and bending moments, greater uniformity of structure, small waste, increased hardness.

But increase of sulphur is greater, due to air obtaining melting temperature a little earlier. If 10 per cent coke is used with 1 per cent sulphur then the percentage of sulphur taken up by solid charging material is 0.05 per cent and in case of briquettes is 0.075 per cent. Borsig gives Table II. to show chemical change of high pressure briquettes.

That the iron had melted "white" is explained by high sulphur and low silicon and carbon percentage. Tests with briquettes of this composition gave the results seen in Table III.

LOSSES OF CARBON.

Results show that briquettes lose carbon when compared with solid materials; that oxidation of silicon and manganese begins only at entrance into melting zone. Tests show that briquettes may be substituted for special irons and be less expensive.

TABLE II.—SHOWING OF THE CHEMICAL CHANGES.

	Total Car.	Sil.	Mang.	Phos.	Sul.	Graph.	C.C.
Pure iron briquettes.	3.60	2.51	0.33	0.50	0.105	2.68	0.72
Melting product	3.04	1.27	0.50	0.44	0.190	0.12	2.92

TABLE III.—BORSIG TESTS OF BRIQUETTES. SULPHUR PER CENT IN THE COKE, 1.0 PER CENT.

	Total Car.	Silicon.	Manganese.	Phosphor.	Sulphur.
Chip briquettes, Borsig.					
Castings from which chips came	3.4-3.8	2.25	0.61	0.60	0.108
Crude iron briquettes, average of 20 pieces.	3.50	2.20	0.64	0.69	0.108
Partly melted briquettes, dropped out in cleaning cupola. Per cent through entire section	3.40	2.20	0.57	0.60	0.118
Same from upper surface to depth of 1.2 inches	3.06	2.16			0.180
Fused iron from briquettes	3.10	1.10	0.48	0.63	0.190

Comparative tests with castings made of ordinary iron and those of 70 per cent cast-iron briquettes gave the results: Ordinary iron, tensile strength, 20,300 lbs. square inch; briquettes, tensile strength, 35,200 lbs. square inch; composition of iron: Si. 3.16, S. 0.115, Ph. 0.46, C. 3.60, Mn. 0.66.

The highest strengths were obtained with castings of the composition given in Table IV.

Tests with Krupp hematite gave results seen in Table V.

There is certainly great economy in use of briquettes. Special irons as those of Frodair, Bearcliff, etc., be-

TABLE IV.—COMPOSITION SHOWING BEST RESULTS.

Sil.	Phos.	Mang.	Sul.	Total car.	Added briquettes.
2.34	0.43	0.58	0.105	3.42	30 per cent.
2.00	0.54	0.58	0.131	3.22	55 per cent.
2.00	0.50	0.56	0.165	3.32	65 per cent.
2.09	0.81	0.61	0.128	3.37	70 per cent.

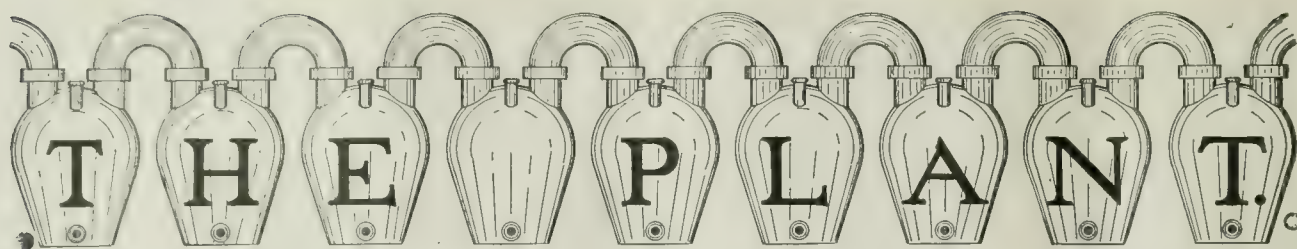
come unnecessary and cost of manufacturing drops without sacrificing strength or quality. If price of Frodair iron is taken at \$28 per ton, that of Bearcliff at \$35 per ton, and that of Coldair at \$24 per ton, then cylinder castings made up to now with these special irons will be made with briquettes and cost will

TABLE V.—TESTS WITH KRUPP HEMATITE.

Sil.	Phos.	Mang.	Sul.	Car.	Steel and cast-iron briquettes.
2.12	0.37	0.61	0.10	3.40	15 and 15 per cent.
1.37	0.30	0.64	0.13	3.40	25 and 15 per cent.

decrease to \$15 or \$16 per ton, and tensile and compressive strength will increase in every case. The briquettes with low phosphorus percentage can take the place of the white iron in malleable castings and in many cases can take the place of the scrap steel.

The clay-working industries of the United States had in 1911 a production valued at \$162,236,181, according to the United States Geological Survey, which has just issued a chart, compiled by Jefferson Middleton, showing the total output, by states, of all the different clay products. The total production of common brick was 8,475,277,000, valued at \$49,885,262. Of this New York contributed the largest amount, namely, 1,143,726,000, valued at \$5,918,286. Illinois was second in output, with 1,074,486,000, but the product had the greater value of \$6,126,911. No other state reached the billion mark. Pennsylvania coming third, with 774,122,000 bricks. The chart gives the figures of production for other kinds of brick—vitified brick, front brick, fire brick, etc.—as well as for terra cotta, draintile, sewer pipe, stove lining, and pottery products. The production of all kinds of bricks was more than ten billion. In total production of clay products Ohio heads the list, with a value of \$32,663,895, or one-fifth of the total for the United States; Pennsylvania is second, with \$20,270,033; New Jersey third, with \$18,178,228; and Illinois fourth, with \$14,333,011.



TANNERY SEWAGE DISPOSAL.

The time when the tanneries of the country can run the wastes from their works raw and untreated into streams is fast nearing an end, and in many localities the question of the nuisance arising from the common practice is already being taken up in various ways such as through the medium of the courts, by means of boards of health, livestock commissions, hunting and fishing clubs and so forth. In a paper read at the Boston meeting of the National Association of Tanners last July, Mr. F. A. Loveland describes as follows a number of methods that have employed in disposing of tannery wastes:

For one tanner to congratulate himself that thus far he has escaped action or complaint against his tannery probably means that the community in which his works are located have been indulgent or apathetic, for sooner or later the broader action of the country or state will reach and embrace him, and make it necessary that some means be provided for the disposition of his wastes other than dumping it into the streams unpurified.

There are probably few tanners who will claim that there is no reason for complaint against the ordinary method of tannery sewage being run direct from the works into the waters of the country in a raw state, for it is commonly known that a tannery is not a rose garden, and that under certain conditions odors might develop from its sewage which would be offensive to delicate nostrils, and possibly prove detrimental to the fish which live in the stream and to animals grazing along its banks and drinking the water therefrom.

Nor is it likely that any tanner would be so forgetful of his duty to his neighbors but that he would be glad to do anything within reason to purify and sweeten the liquid wastes from his plant, knowing that by so doing he would also make for better conditions for himself and workmen.

So far as conditions about the ordinary tanning plant are concerned, probably not much criticism can be made as to its not being kept in a sanitary state, for most tanners will undoubtedly concede that one of the essentials, for making a good product is clean and wholesome conditions in and about the plant.

Sometimes unjust criticism is made against necessary tannery odors, for there are odors about some industrial plants which are characteristic of the industry and cannot be avoided, like slaughter houses, rendering plants and fertilizer works, and about the tannery the smell of tanning liquors and hides and

skins will probably always continue, and complaints about them are naturally beside the mark.

The successful treatment of tannery sewage presents a problem difficult to solve because of the character of the wastes. Where the sewage requires to be pumped in order to receive treatment, it is found that the pumps become easily and seriously clogged with the hair and flesh which find their way into the sewage, even when great care is taken to prevent their entrance. The salt and dirt which is washed from the hides mixes with lime and hair, forming a sort of cement which is apt to obstruct the sewers carrying the sewage to the treating tanks.

Perhaps no tanner would own to wasting any considerable amount of his tannin, yet careful as he may be there is sufficient present in most tannery sewage to produce a dark color to the water into which the effluent flows, especially where traces of iron are present in the water.

Where a fine filtering media, like sand, is used, the lime soaps and fats present in the sewage and carried past the precipitation tanks, soon clog the pores of the filter and make it useless. Even though the effluent may be of fair character when it enters the stream, the soluble solids it contains soon decompose and deposit these solids in a light, flocculent form on the bottom and along the sides of the stream, making an unsightly appearance, and causing offensive odors in warm weather. Where precipitation tanks are installed it is found that the sludge is difficult to free from water so as to handle cheaply and quickly in the cleaning of the tanks, and in carting away.

It has also been claimed that tannery sewage, when mixed with ordinary city sewage, makes the whole more difficult of treatment in municipal treating works, an English tanner stating that he was imposed an additional tax for this reason, also because it was claimed that the character of his sewage was such as to cause a slow deterioration of the material of which the sewer was composed into which his effluent flowed. The foregoing are, perhaps, the chief items which go to make up the problem as a whole, though others may readily occur to some of you in connection with the problems of your individual plants.

Perhaps it would be of interest to note some of the methods in operation in plants where attempts are being made to purify the sewage. One large tannery has a series of four settling vats, built about 3 or 4 ft. above grade, into which the sewage is pumped. These

vats are built so as to be operated in series, and so arranged that any one can be cut out for cleaning while the others remain in operation. They are built above ground so the sludge can be readily loaded into a wagon-box from an opening in the side of the vat being cleaned. From these vats the sewage goes to the stream.

Another tannery pumps the sewage to a high point of ground from whence it flows to the stream over a series of dams, thus allowing the solid matters to settle and collect in the pockets behind the dams. A resident near the tannery in describing this method said the odors were quite pronounced in the heat of summer, caused probably by the decay of putrescible matters held back by the dams.

Another tannery had a large vat built in which was constructed a false bottom of heavy wire cloth. The sewage is run into this above the false bottom, and then pumped from below the wire screen into a tank or leach partly filled with spent bark, and after filtering through this medium is run to the stream.

Another method in use by a large tanner is to run the sewage on to filter beds about 30 ft. x 5 ft. deep made up of screened cinders. Several of these beds are laid down, so when one becomes obstructed it can be cut out, cleaned, redressed and made ready for service while others are in operation.

A method tried out by a large tanner having around a million gallons of daily sewage, was to construct a series of settling or precipitation vats, four in number, supplemented with a series of sand filters. The sewage was first run into the settling vats to deposit the hair, flesh, lime and other heavy solids; thence over the sand filter beds and to the stream. This method proved a failure in practice for it was found that the lime soaps and fats, carried past the settling vats, soon clogged the sand filters to such an extent as to make them useless. This part of the system was then abandoned and the settling vats alone retained in operation.

Another plant having about 100,000 gals. daily sewage has been under experimental work in connection with the health department of its state for some time and the following report from the state department may prove of interest as it bears directly on this question:

The state department of health has made investigations and experiments in co-operation with your company for the treatment of liquid wastes at your tannery. It appears that the solids in the waste at your tannery can be separated from the liquids at a reasonable cost. The putrefactive bacteria can be destroyed by double filtration, the expense for installation and maintenance being very high.

An acre of sand filter would be required and its cost would be approximately \$15,000. The straining of the settled effluent would be necessary and a double pumping also. Probably the outlay for installation would not be less than \$20,000. This process should filter out the anthrax germs, but not necessarily destroy them. They would be retained in the filter for indefinite periods.

A stable effluent can be secured and all *B. coli communis*

be destroyed by the use of chlorinated lime and the cost of doing this is within the means of your company. However, this will not kill the anthrax germ. After subsidence and straining through a rough filter, the effluent might be passed through a mechanical filter whose object would be to retain the anthrax spores. The waste wash water from cleaning operations would be small in bulk and could be evaporated in the boiler under 60 pounds pressure or more, which would assure the destruction of the spores. By this process, which would come within your means, and by the use of bleach a stable effluent would be secured, the colon would be destroyed and the anthrax germs would also be eliminated.

The sludge should be reduced to dried, inflammable material by a centrifugal dryer and then destroyed by fire under the boilers, such as is the practice in a number of sewage disposal works in this and foreign countries.

The straining or roughing filter between the subsidence tank and the sand filter would be small in area and might be economically built of porous asbestos. The advantage of this construction would be that the strained out materials could be subjected to combustion without removal from the layer of asbestos, by use of an overhead flame. In the tests conducted by the department and your company, where the treatment by the use of chlorinated lime of the whole waste of the tannery was accomplished, the odor of chlorine was detected for four miles below the tannery. The offensive odors along the stream, about which complaint has been made for several years, were thus effectively reduced.

It is suggested that you install apparatus for the disinfection, by hypochlorites of lime, of the entire waste output of your tannery. That the sedimentation tank be enlarged in order that there may be a period of four hours' sedimentation before the introduction of the chemical solution to the tannery waste is effected and so that four hours of contact may always be secured after the chemical solution has been added.

That duplicate sewer connections be made to the pump well in order to obviate any discharge of tannery waste into the stream; that the flow from the works to the sedimentation tanks should be regulated so as to render the delivery into the sedimentation tanks more uniform.

That a roughing filter with facilities for cleaning should be installed at the outlet of the tanks to intercept suspended matters not settled out of the sewage. The type hereinbefore mentioned might be used to advantage. A sand filter of mechanical type should be established as a finishing process. This secondary filter should be provided with facilities for cleaning and the wash water should be collected and evaporated on not less than 60 lbs. pressure. And, finally, the sludge from the treatment works should be collected and treated in the centrifugal dryer and be destroyed by fire.

In England the question of tannery sewage has, perhaps, been gone more thoroughly into than elsewhere, possibly on account of the dense population, and there the general method is about as follows: A series of precipitation tanks followed by filter beds made up of coke, coal, cinders or other cheap media, followed by a series of catch tanks, then to sewer or stream. In some plants the settled sewage is run over these filter beds till a bed becomes clogged, then this bed is cut out and allowed to stand for a time to become dry, when it is cleaned of surface accumulation, redressed with additional media and placed in service again. In our own experimental bed we found that the time of service was about three to four weeks, when by removing 3 or 4 inches of the surface and redressing, the bed would be effective again for about the same period.

Another method sometimes used where conditions are favorable is to plow a field into wide furrows and allow the sewage to run into these furrows and slowly seep the liquids away while the solid matters remain. After a time the first field is put under cultivation and a second put into commission.

The following extracts from a report on the sewage disposal system at Litchfield, England, should prove of interest, as it is understood this system follows closely the general method for the treatment of tannery sewage in that country.

The treatment of Litchfield sewage is one of difficulty because of the large amount of trade waste discharged. The system is of the continuous flow type. There are two sets of precipitation tanks of a combined capacity of 244,650 gals. There are a total of twelve filters of a superficial area of 4,712 sq. yds., and a cubical content of 7,460 cu. yds. The depth of the filters varies from 4 ft. to 5½ ft. In other words, the twelve filter beds are about 60x60 ft. and about 5 ft. deep.

The medium of the filters, with one exception, is coal and made up as follows: 1 ft. in depth with coal 2 in. to 1 in. in size, and the balance with coal ½ in. to ¼ in. in size. One filter bed was made up with slag in March, 1908, as follows: 6 in. deep with slag 2 in. to 1 in. in size, and 3 ft. 3 in. with ¼ in. to ⅛ in. in size. This filter has been worked ever since and at present shows no signs of deterioration or pooling. The top 9 in. of the coal filter beds is being gradually replaced with slag, as it is found that coal is inclined to disintegrate when exposed on the surface.

The system of distribution of sewage is by means of fixed sprays. About 72 tons each of aluminoferric and milk of lime are used per annum as precipitants. The effluent is generally of good quality, but inclined to deteriorate when mixed with the brook water, with the result that a considerable quantity of flocculent matter and sewage fungus collects in the brook. The dry weather flow of sewage is at the rate of 400,000 gals. for 24 hours, or 45 gals. per head of population. Most of the solid matter is removed in passing through the precipitation tanks. The precipitants (alum and lime) are added after the sewage has passed through the precipitation tanks and consequently very much better results are secured than when precipitants are added to the raw sewage, besides saving about 75 per cent of the precipitants. In summer the sewage has about 6¼ hours, and in winter about 10 hours in passing through the precipitation tanks.

In concluding, it might be well to remark that probably no system of tannery sewage disposal which shall meet the requirements of and be passed by the state authorities, can be installed without considerable cost and that the operation of the same will prove both expensive and troublesome. It is understood that the English types of disposal systems, which are perhaps the best, give considerable annoyance and present difficulties of operation that requires constant

vigilance both from the tanner and the authorities to keep them properly working, so as to deliver an effluent good in character to the streams. It is unfortunate that no general system of tannery sewage disposal has been passed upon by any of the states, so that a tanner is placed in the unfortunate position of being pressed to do something with his sewage, and not knowing what to do or whether it will be acceptable if he makes an attempt to work out the problem.

It would seem a matter of importance that the National Association of Tanners try, in conjunction with the state authorities where tanneries are numerous, to work out a general system of tannery sewage disposal which would be acceptable to the officials, workable, and within the reasonable means of the tanner to install and operate with a minimum of trouble and expense.

The American Cyanamid Co., of Niagara Falls, Ont., has contracted with a Boston, Mass., construction firm for the erection of an extension to its plant, which, when completed, with machinery installed, will cost approximately \$500,000 and will more than double the present capacity. This company, operating by the Frank & Caro process (German), manufactures a nitrogenous fertilizer material, the nitrogen of which is derived from the atmosphere (the fixation of atmospheric nitrogen). The process consists of the nitrification of calcium carbide made from coke and lime in an electric furnace, which process takes free nitrogen from the air, fixing it into a form available for plant food. The cheap and reliable hydroelectric power available at Niagara Falls makes it possible to generate the intense heat necessary to accomplish results, and at present the company uses 6,000 electric horsepower. It began the manufacture of cyanamid in January, 1910, and during that year exported to the United States product valued at \$211,202. In 1911 the invoiced value of the cyanamid shipped to the United States was \$338,774, an increase of \$127,572; and, judging from exports so far invoiced during the present calendar year, the increase will be much greater, making the addition to its factory necessary to keep pace with the growing demand.

The U. S. Consul at Georgetown, British Guiana, states that books painted with the following compound on their receipt in the tropics, and every three to six months thereafter, are rendered exempt from damage by the ever-present cockroach and much less liable to attack by wood ants and silver fish. They should be painted all over the outside when closed and inside thoroughly at the seam of both front and back covers. A strip 2 to 3 ins. wide should also be painted on the inside edges of the covers. In this manner, with a little trouble and trifling expense, the archives can be kept in good condition. The formula is as follows: Corrosive sublimate, ½ ounce; carbolic acid, 1 ounce; methylated spirits, 2 pints. Label "Poison."

THE TESTING OF CLAY REFRACTORIES.

This technical paper from the Bureau of Standards of the Department of Commerce and Labor, was prepared under Director Stratton by A. V. Bleininger, Ceramic Chemist, and G. H. Brown, Assistant Ceramic Chemist, respectively. The full title is, "The Testing of Clay Refractories, with Special Reference to Their Load Carrying Capacity at Furnace Temperatures."

The authors first speak of the object of the paper, stating clearly that it is confined to the clay refractories exclusively, without considering other refractories such as silica or magnesite. Whatever the strength of a clay brick may be at ordinary temperatures, its strength will be an entirely different quantity at the elevated temperature at which it will be used. Thus a temperature can be attained at which the brick will not even support its own weight, this temperature depending on the lowering viscosity of the substance as it approaches the temperature at which it fuses. The rate of closing of the pore spaces, the presence of fluxing oxides, and the conditions of stress and strain determine the temperature at which the deformation shall take place. The point of the paper is to study the conditions decreasing refractoriness and how to know the different materials by laboratory tests.

The authors have evidently done their work thoroughly and well. The results will appeal strongly to all those engaged in chemical engineering or metallurgy who might ever need to use this kind of refractory material. Scientific data is all too meager and this will be acceptable as a contribution, especially useful to those who are at work applying their knowledge in the industries.

The nature of the refractory clays is given chemically as approximating to the formula of the hydrous silicate of alumina:



and divided according to physical properties as kaolins, flint clays and high-grade plastic clays; the latter generally decreasing in purity and of plastic properties at the expense of heat-resisting power.

Under the topic of manufacturing refractories it is explained how the clays should be mixed for practical work.

The fusion of clays is then discussed in considerable detail; Seger cones are mentioned and compared, the formulas and softening temperatures of the higher numbered cones being given.

In discussing the specific effects of heat on clays the authors take up dehydration, contraction, the crystallization of sillimanite from the clay and the final softening. Then the effect of adding quartz, alumina, titanium oxide, iron oxide, the alkalies, mica, lime and magnesia is indicated, all of these but alumina decreasing the refractoriness. Alumina increases the refractoriness but also the contraction unless fused

alumina is used. The combined effect of the different fluxes is then discussed from the theoretical side.

The actual laboratory investigation concerned the testing of more than 35 brands of fire brick as well as other clay products. Upon these samples load carrying tests of 75 lbs. at 1,300° C. and 50 lbs. at 1,350° C. were carried out and checked with accurate chemical analyses, cold crushing strength, softening temperature, porosity and true density.

Passing over the numerous tables, diagrams and photographs of the results which form the basis of comparisons, methods of improving and specifications, every detail of which will be of value to those interested we may well quote the final conclusions:

"The load test described in this paper furnishes a criterion of the viscosity of refractories and, therefore, of their load-carrying capacity at furnace temperatures. It has been found that the softening temperature of fire-brick specimens is not a safe criterion of the "standing-up" quality of fire-clay products. The ability to withstand a load test at 1,350° C., with a compression of 50 pounds per square inch, estimates the refractoriness of a material under working conditions. Failure is considered to have taken place when the specimen shows marked deformation or contracts more than 1 inch, referred to the standard length of 9 inches.

It was found that a content of more than 0.22 equivalent of fluxes results in failure in the load test, with a silica content varying up to $1\text{Al}_2\text{O}_3 : 3\text{SiO}_2$. With a higher content of silica the permissible RO seems to decrease. Thus with 4.4 molecular equivalent of silica an RO content of 0.17 equivalent may bring about failure.

It has been shown that bond clays of inferior refractoriness can be improved by thorough grinding with flint clay or some other heat-resisting material, low in fluxes.

Refractories should be burned to as high a kiln temperature as possible, at any rate not below cone 10 and better at cone 12.

A good initial compressive strength is desirable for bricks subjected to load conditions. When tested on end (at atmospheric temperature) a crushing strength of more than 1,000 pounds per square inch is required.

The load test can not be taken as the sole criterion of the value of a refractory, but the softening temperature and the chemical analysis must likewise be considered.

While the load test is important for industrial practice, since conditions of direct and transverse compression and extension exist under nearly all furnace conditions, it is less valuable where the loads imposed are insignificant.

Tentative specifications for No. 1 and No. 2 refractories have been suggested.

H. B. P.

POTASH AND IODINE FROM SEA WEED.

Considerable space in the technical press has been devoted recently to a discussion of the possibilities of obtaining potash salts from sea weed. In view of the importance of the matter the following letter of Henrik Knudsen, appearing in a recent issue of the Journal of Industrial & Engineering Chemistry, is of particular interest.

In Senate Document No. 190, 62nd Congress, 2nd Session, "Fertilizer Resources of the United States," as well as in an address by F. K. Cameron,¹ sea-weed and especially that of the Pacific coast is mentioned as a possible source of the potash salts used in the United States.

Most of the Senate Document consists of an ordinary description of the stationary growing algae (kelps) and their ecological character. Much space has been given to the species of *fucus* growing in the litoral region. Every expert knows that this species of no value, as these plants absorb very little valuable material.

The content of inorganic valuable materials in these kelps depends first of all on the physical conditions of their growth. Force of current, temperature, and content of salts are important factors, but other life conditions of the algae also affect their chemical composition. It is of considerable importance whether they are growing near the surface or in deeper water, in comparatively quiet straits or in the breakers of the ocean. The species which, while growing, absorb the most valuable materials are not found in any considerable amounts in the straits or sounds² nor in the litoral region, but are abundant out in the ocean, and about the belts of islands, girding the coast, and in these places from the limit of tidewater down to the depth of 20-25 fathoms.

The far more important "Porra" which, until lately, has been given very little consideration, deserves, technically, the greatest attention. A flourishing sea-weed industry on the Pacific coast can be imagined only on the basis of this marine plant. It grows in deeper water and in the open ocean and is consequently richer in valuable materials. It is found in great abundance, is easy to harvest along the coast during fall and winter, and can be worked at proportionately lower cost.

The Senate Document, furthermore, suggests some antiquated methods of burning sea-weed, of preparations of potassium salts, and finally of "Methods of Analyses."

I should advise the use of the "kelpash" and its contents of inorganic valuable materials as the standard scale for the valuation of sea-weed, and not the sea-weed itself. This will simplify transactions between the seller and buyer of kelp or kelpash.

Far more interesting are the colored charts, copies of the U. S. Coast Survey Chart. They ought to be

combined but they should indicate the special places along the coast, where the "driftkelp" is washed ashore by the stream. As the explorations are limited to the few summer months and as this season mainly comprises all kinds of stationary growing kelp, the useful as well as the useless, we are able to find in the Senat Document little of any importance from which to form any opinion about an eventful lucrative sea-weed industry on the Pacific Coast.

The conclusion drawn from these preliminary explorations is that in the sea-weed of the west coast we have not only a source to furnish all the potash salts consumed in this country but "it means a possible production of potassium chloride about the same as, or even a little larger than, the total production in Germany," and, "taking every consideration and leaning strongly to conservatism, it might be said that it ought to be perfectly practicable to obtain an annual yield of at least a million tons of potassium chloride, worth at present prices, upwards of \$30,000,000. The iodine obtainable at the same time should go far toward paying the expenses of harvesting the kelp and extracting the potash."

In the opinion of the writer, \$30,000,000 a year, made by potash and perhaps a similar amount or more by iodine extracted from sea-weed on the west coast of the United States, is surely impossible in the light of the following analysis:

1. Is it possible that the Pacific sea-weed can produce sufficient raw material for the production of one million tons of potash salts?

2. Can the potash salts obtained from sea-weed containing a limited quantity of iodine (not more than $\frac{1}{2}$ per cent in the ash of the plant) be furnished at a price similar to that of German potash salt?

To answer the first of these questions, I need only point to the simplest and primitive method of producing (burning) kelpash on the shore. The proposed technical improvements in this process have as yet never been tried practically, and do not promise any such profit as suggested in the published statements.

For the purpose of illustration, I shall use the *Nereocystis Lutkeana* mentioned in the Senate Document among Dr. J. W. Turrentine's "Analyses of Pacific Kelp," Sample No. 8. This marine plant (a laminaria) belongs to those containing the largest quantity of both potash and iodine. It is found, as far as known, in the largest quantities at the northern part of the Pacific Coast. The dried plant contains 46.2 per cent organic matter, 51.3 per cent soluble salts and 2.5 per cent ash. Of the soluble salts 23 per cent are actual potash (K_2O) and 0.17 per cent iodine. The total amount of ash of this plant is 53.8 per cent. The contents of the ash are then 42.7 per cent actual potash (K_2O) corresponding to 67.7 per cent potassium chloride (KCl) and 0.316 per cent iodine.

If we take the above mentioned quantity of ash as a basis, we find that it requires for the production of 1,000,000 tons of potash salts: 9,724,500 tons of wet

¹Journal of Industrial and Engineering Chemistry, 4, 169.

²For the last 10 years, I have known the kelp from the interior part of Puget Sound to be of very little, or no value.

sea-weed, containing 80 per cent water, representing 1,048,900 tons of dried sea-weed, producing 1,048,500 tons of ash, representing 1,000,000 tons mixed potash salts.

I presume of course that the whole quantity of soluble salts is extracted as potash salts. This is indeed what is done in practice, as it is quite impossible in a huge production, as the one mentioned, to crystallize the salts singly. Of the potash present, half the quantity will come out as 80-90 per cent potassium chloride and the other half will consist of a "mixture" of chlorides, carbonates and sulphates, mostly of potassium, sodium and a little part of magnesium containing about 16-20 per cent actual potash (K_2O), corresponding to the German manure salts, Hartzsalt and Kainit.

For one million tons of potassium chloride, we shall have to multiply the above mentioned amount of sea-weed and kelpash by two.

I presume that these figures will convince everybody that it is impossible to reach a production of a million tons of potassium chloride on the basis of the sea-weed of the west coast. To furnish entirely the large quantity of potash salts consumed in this country, the United States will have to find other "deposits." It might be of interest to note that the necessary quantity of kelpash containing 0.316 per cent of iodine, used for the production of a million tons of potash salt, will furnish 7,400,000 lbs. iodine, valued at the present price at \$14,000,000 or many times more than the total yearly consumption of the world at present.

Now let us see at what price this kelpash may be produced and how great an army of laborers the production of 1,048,500 tons of kelpash will require.

If the season on the Pacific Coast allows 150 working days for the harvesting and burning of the sea-weed, it will be necessary to produce 7,000 tons of ash a day. If one man produces 200 lbs. of kelpash per day,³ at a daily wage of \$2.00 (on the west coast this is rather low), the ash will cost one cent per lb. or \$22.40 per long ton. This is at the present time the average price of kelpash in Scotland and Norway.

The production of 7,000 tons of ash a day for 150 days will require 7,800 men, for only the harvesting, drying and burning of the sea-weed on the shore. For the production of 1,048,500 tons of kelpash twice the number of laborers will be needed. The figures given speak for themselves. I will only add that in practice, conditions will surely be in all respects much less favorable than here anticipated.

The second question, the price of sea-weed potash in competition with German potash, will probably not be any more convincing. Yet this is a more favorable case because we are able to calculate the expense of the production, based on the contents of valuable materials as published in the Senate Document.

³A man will have to cut, bring ashore, dry and burn about one ton of wet sea-weed.

Continuing with the favorable marine plant, sample No. 8, *Nereocystis Lutkeana*, I figured as follows:

Harvesting and burning, per ton ash.....	\$22.40
Freight and other expenses in handling the ash from the coast to the plant, estimated, per ton.....	2.00
Expenses of production per ton ash:	
Coal	\$ 3.90
Labor	4.50
Chemicals	1.00
Salt bags	2.00
Commission on the sale of potash and iodine	1.50
Administration, etc.....	1.00
Interest and depreciation.....	2.50
Sundries, taxes, etc.....	1.00
	16.50
Total cost per ton ash.....	\$40.90
0.316 per cent iodine = 7.08 lbs. per ton ash at 6 pence per ounce (present price).....	11.20
95.3 per cent soluble salts, 2134.6 lbs. per ton; of this 1067.3 lbs. are potassium chloride (80-90 per cent KCl), according to German price \$35 per 2000 lbs. net.....	18.67
And 1067.3 lbs. are manure salt (20 per cent K_2O), according to German price \$13.30 per 2000 lbs. net	7.09
Selling price per ton ash.....	39.96
Loss per ton ash.....	\$ 0.94

Even if all the potash present could be extracted as potassium chloride (which is impossible) it would make only an insignificant improvement on the figures of cost given. The above mentioned expenses are based on a personal experience of more than 20 years.

In practice the aspect will be far more unfavorable than pointed out above, because I have presumed here that the whole quantity of potash salt as well as iodine could be extracted.

A potash industry on the basis of sea-weed will first and last depend on the content of iodine in the marine plants.

One-tenth of 1 per cent more or less of this valuable material is the kelpash can change the production from a valueless to a very remunerative business. It is certainly also very important that all of the valuable products in the plants, the organic as well as the inorganic, be utilized.

It is my opinion, nevertheless, that a great and very profitable industry could be founded if the contents of iodine in some of the species of *Laminaria* on the west coast prove to be satisfactory, but not an industry of any such dimensions as suggested.

Besides the content of iodine, it is of the greatest importance to use the best methods in handling the raw material as well as in the extraction of the products, and furthermore, to utilize to the utmost the valuable materials of the marine plants, both organic and inorganic.

As yet we possess very little of value and very little authentic information to solve the question "Is it possible to build up a *lucrative* industry on the abundant growth of sea-weed at the Pacific Coast?"

The value of the brick, tile, pottery, and various other clay products made in Massachusetts in 1911, according to the United States Geological Survey, was \$1,700,287. This is almost the exact figure of production as reported for the preceding year.

THE SLAGGING TYPE OF GAS PRODUCER, WITH A BRIEF REPORT OF PRE- LIMINARY TESTS.

The gas producer is to-day receiving wide attention from mechanical and chemical engineers, and general interest is shown in any experiments to determine its utility in power plants as a means of reducing the cost of fuel. In view of the importance of the problem the Bureau of Mines is conducting a series of investigations to determine the value of the slagging type of producer in the utilization of high-ash fuels and the conditions under which this type is most satisfactory. Tests have been made with coke, with limestone as a flux, for intermittent and for continuous runs up to 100 hours, and the results obtained give promise that high-ash fuels may be successfully utilized in this type of producer. A report on these preliminary tests is embodied in a technical paper issued recently by the Bureau of Mines. The paper was prepared by Mr. Carl D. Smith, and is given in abstract below:

Producer gas consists necessarily of a mixture of several distinct gases, of which some are combustible, the rest non-combustible. In the generation of producer gas it is desirable to maintain as high a percentage of combustible gases as is consistent with efficient operation. The principal combustible in producer gas is carbon monoxide. This is a colorless, odorless gas, and is a product of incomplete combustion in which the carbon combines with one-half the oxygen that is required for complete combustion. The formation of this gas takes place when air passes through a thick fuel bed of incandescent coke or carbon and probably according to the formula



As a result of laboratory experiments on the rate of formation of carbon monoxide, it has been shown that, for the production of high percentages of carbon monoxide, the producer fuel bed should have a temperature of 2,300° F. or over, and that by operating at these temperatures the capacity of the producer would be greatly increased.¹ In usual practice, however, great care is taken to prevent such high temperatures in order to avoid fusing the ash and the consequent serious clinker difficulties. High temperatures are thus very desirable on the one hand, whereas on the other they are undesirable, and with coals having an easily fusible ash, they may be a great disadvantage. In general, the result of these conflicting conditions on the operation of producer plants is a compromise in which the temperatures maintained are as high as the character of the ash permits without fusion and the formation of objectionable clinkers.

In an effort to obtain the advantages, as well as to avoid the disadvantages resulting from high temperatures in producers of the usual type, tests with a

producer of the blast-furnace type, or a slagging producer, were suggested early in the history of the bureau. In such a producer ash can be removed as a liquid slag, and it was believed that fuels containing a high percentage of ash could be thus utilized, and that the accompanying temperatures would be ample for the production of a high percentage of carbon monoxide. The slagging type of producer was therefore selected for the investigation discussed in this paper.

The slagging or blast-furnace type of gas producer was among the first made. Bischof is usually credited with the first internally fired gas producer, built in 1839, and only a year later, in 1840, Ebelmen built the first slagging producer at the iron works of Audincourt in France. Charcoal was the fuel used. Iron-furnace slag and clay were charged into the producer with the fuel. This formed with the ash an easily fusible slag which ran off at the bottom of the hearth. For several years following there seems to have been no development in producers of this type. The "Transactions" of the American Institute of Mining Engineers for 1881 contain a brief description of a slagging producer built by W. J. Taylor and operated in Chester, N. J. Very satisfactory results were reported, as follows: Gas of excellent quality, uniformity of operation, uninterrupted service (four weeks' operation without any shutdown being cited), and ash easily removed as a liquid slag. Small sizes of anthracite were used for fuel, and 30 to 40 per cent of blast-furnace slag was added to flux the ash. There seems to be, however, no record of any results from subsequent operation, and information as to success or failure is not to be found. At any rate the producer seems to have dropped out of use, while the development of producers of other types continued.

A more recent application of the blast-furnace type in producer design is found in the development of the "S. F. H." gas producer in France. This producer is reported to be operating satisfactorily and giving excellent results. Ash is removed from time to time as a liquid slag, the gas is of good quality, and low grades of fuel are said to be readily gasified.

In a description of this producer the following statements are made:²

The slagging type of gas producer permits excellent utilization of the fuel. The composition of the gas is almost constant for a given fuel and its calorific power is extremely regular.

The S. F. H. gas producer permits the utilization of all kinds of fuels, particularly wastes, refuse coal, breeze, coal cinders, etc., the only condition being that they have a content of fixed carbon sufficient to develop heat enough in gasification to distill the volatile matter, to vaporize the contained water, and to fuse the ash.

It is also stated that the amount of heat required to fuse the ash is exceedingly small and is much less than the heat value of the carbon lost in the ash from producers having grates. Reference is made to a

¹See Bulletin 7, Bureau of Mines, Essential factors in the formation of producer gas, by J. K. Clement, L. H. Adams and C. N. Haskins. 1911. 59 pp.

²Sepulchre, M., Notes on the S. F. H. gas producer, cleaned by fusion of the cinders. *Revue de metallurgie; mémoires*, vol. 6, p. 730.

"suitable flux for fusing the ash," but no statement is given as to what it is.

A battery of these producers, installed at the glass-works at Gironcourt-on-Vosges, in 1907, furnishes gas for several large plate and annealing ovens and, as is reported, in a most satisfactory manner. An analysis of the fuel used is given as follows:

Constituent.*	Per cent.
Moisture	15
Volatile matter	25
Fixed carbon	35-40
Ash	20-25

*The sulphur, 6 to 7 per cent, chiefly in the form of iron pyrites, was determined separately.

An analysis of the gas is reported as follows:

Constituent.	Per cent.
CO ₂ and SO ₂ (determined together).....	2-3
CO	28-30
H ₂ and CH ₄	9-10

Results like the above are at once seen to be very creditable, and show a satisfactory utilization of comparatively low-grade fuel. If it is found that the low-grade fuels of the United States can be utilized economically in a commercial way in producers of this type, and should the use of these producers become general where such fuel is available, a great saving in the better grades of coal would result.

The equipment installed for the investigation now in progress by the Bureau of Mines consists of the producer, a scrubber, gas meter, blower, preheater, steam boiler, and such scales, thermometers, thermocouples, and gas-sampling devices as are necessary.

The producer consists of a cylindrical steel shell lined with brick and provided with a slag notch, through which the liquid slag is tapped off. Near the base of the producer are six air tuyères, and, in addition to these, four separate tuyères are provided at points above the air tuyères, through which steam may be admitted. Fuel is charged at the top of the producer and the gas passes off through the side at a point near the top.

Because of the extremely high temperatures that prevail in the combustion zone, it has been necessary to provide a special cooling device in order to prevent the brick lining from melting and fluxing with the slag. For this purpose a water-cooling arrangement was devised consisting of a coiled pipe embedded in the brick lining. Between the coil and the fire is a 4½-inch layer of magnesite brick. This cooling coil extends over a space of about 20 in. just above the air tuyères. The air and steam tuyères are of cast iron and extend through the brick lining to the fire, but they are water cooled and thus protected from the intense heat. Steam, however, does not come in direct contact with any water-cooled surfaces and consequently there is little, if any, condensation in the steam tuyères. The top of producer also is water cooled and thus protected from the intense heat.

The scrubber consists of a cylindrical shell containing numerous water sprays, but no baffle plates nor layers of coke. Gas enters at the bottom of the

scrubber through a water seal, passes upward through a dense spray or fog, and finally through a layer of excelsior, which acts as a dry scrubber. From the scrubber the gas passes directly to a large gas meter.

The air blast for the producer is furnished from a blower of the positive-pressure type. The quantity of air used depends upon the rate of fuel consumption, and is controlled by a regulating valve through which a part of the blast may be by-passed to the atmosphere. The air-blast pressures in the tuyères also vary according to the rate of fuel consumption, from 5 or 6 in. of water to about 16 inches at the higher rates. Steam is supplied as desired at definite rates by a small gas-fired boiler. Preheating of the air blast is accomplished by passing the air through a heater in which a portion of the gas produced is used for fuel.

In order to establish a fundamental basis to which the results of subsequent tests may be referred, the first tests have been made with coke, a fuel nearly elementary in character, with which complications due to the volatile constituents of bituminous coal are avoided. Tests will be made, however, of different grades of bituminous coal as well as tests of high-ash coals. Although the investigation on the utilization of fuels in a slagging producer includes tests to determine the effect of different operating conditions, several preliminary tests have been made to determine the feasibility of melting the ash and removing it from the producer as a liquid slag.

The readiness with which a fuel ash will melt and form a fluid slag depends upon the relative percentages of its constituents and the temperature to which it is subjected. Usually the desired fluidity is increased by the addition of a flux such as limestone.

In the preliminary trials with the slagging producer the coke used contained about 11 per cent of ash, and in order to make a more liquid slag limestone crushed to about ½-in. size was added to the coke charge.

Analyses of both the ash and the limestone are given in the following table:

Analyses of Coke Ash and Limestone.

Constituents.	Ash.*	Limestone.*
Silica (SiO ₂)	54.83	1.73
Alumina (Al ₂ O ₃)	31.94	.93
Ferric oxide (Fe ₂ O ₃).....	7.22	.80
Calcium oxide (CaO).....	2.06	52.20
Magnesium oxide (MgO).....	.25	1.48
Potassium oxide (K ₂ O).....	1.49	.00
Sodium oxide (Na ₂ O).....	1.04	.00
Loss on ignition.....	1.19	43.28
Total	100.02	100.42

*Analysis of ash by F. M. Stanton; analysis of limestone by A. C. Fieldner.

Although computations were made from these analyses for the amount of limestone required to produce the more readily fusible slags, the results from the use of the calculated amounts were unsatisfactory. When the producer is in operation large quantities of fine coke ash blow over with the gas because of the heavy air blast, and it is probably true that some of the limestone is blown over in the same manner. At

least on one occasion practically all of the coke ash and limestone escaped in this way. Under these conditions computations from the analyses were of little use in determining the necessary limestone. The problem has been one of trial rather than calculation, and tests have been made with different amounts of limestone, varying from 4 to 28 lbs. per 100 lbs. of coke charged.

Use has also been made of a triangular slag diagram which is the result of work on slags and slag fusion temperatures by Boudouard. From this diagram the approximate fusion temperatures may be found for different percentages of the three principal constituents of slag. There seems to be some question, however, as to whether a slag in which the proportions of these constituents are such as to give a low-fusion temperature is, at the same time, one which will be least viscous or most fluid as the temperature increases.

In the first trial made, about 30 lbs. of coke was burned per square foot of fuel-bed area per hour, and to each 100 lbs. of coke charged, 6 lbs. of limestone was added; the fuel bed was maintained at a depth of 6 ft.; no steam was used, nor was the air preheated. The ash and limestone fused into a pasty mass at the bottom of the producer, and when the slag notch was opened the semifluid slag flowed out very slowly; it was exceedingly sticky, solidified quickly and presented when cold a black, glassy appearance. Throughout the day of the first trial the slag continued to have the same general characteristics, being black and sticky, but it did not, apparently, accumulate or solidify in the producer. Toward the latter part of the day a sample of gas was taken as a matter of interest; this sample, when analyzed, showed 31 per cent CO and less than 2 per cent CO₂.

From the slag diagram of Boudouard the amount of limestone required to make up a slag having a low-fusion temperature was only 4 lbs. per 100 lbs. of coke. A test was made with these proportions but the results from a slagging standpoint were unsatisfactory. The slag was very sticky and would hardly flow from the producer. During this trial no steam was used and the air blast was at room temperature. After a few hours' run the slag began to solidify within the producer, the test was stopped and the fuel bed immediately dumped. The bed was dumped easily, but in the bottom of the producer there was an accumulation of clinker 6 to 8 ins. deep which was very sticky, and the removal of this required considerable effort. The quality of the gas was satisfactory, being high in CO and very low in CO₂.

Trial runs with 12, 20, and 28 lbs. of limestone were made under the same conditions of operation, namely, no steam, air blast at room temperature, and fuel bed at a depth of 6 ft. With 12 lbs. of limestone per 100 lbs. of coke fair results were obtained; the slag was still a little sticky and black, but it ran freely from

the producer and there were no evidences of clinkering or of slag accumulation. With 28 lbs. of limestone the maximum amount that would form a fluid slag was undoubtedly passed. In this case the slag presented little fluidity and completely solidified soon after leaving the producer. At the close of the trial a mass of clinker 4 to 5 ins. thick was found on the producer bottom; it was very brittle, however, and was easily broken to pieces and removed. In a trial with 20 lbs. of limestone per 100 lbs. of coke satisfactory results were obtained, the slag being much less viscous than on any preceding trial; it ran from the producer very freely and remained sufficiently liquid to spread over a considerable area before solidifying.

In attempting to operate the producer intermittently—that is, with the fire banked at night—considerable difficulty was experienced from the accumulation of clinker during the shutdown, more especially when a cold-air blast was used. After shutdowns of one night the producer has been started a number of times on cold air with satisfactory results, but with more than one shutdown there were excessive clinker accumulations. With preheated-air blast, however, a 4-day intermittent run was made possible. Some clinker accumulated, but gas of good quality was produced throughout the entire operating time. A producer of the blast-furnace type can hardly be expected to operate intermittently because of its inherent tendency to “freeze” during shutdowns.

Continuous runs of from 75 to 100 hours have given very satisfactory results, both as regards the character of the slag and the quality of the gas. In one test of 76 hours' duration the gas produced was uniform in heat value and of very good quality, averaging for the run about 31 per cent CO and less than 1½ per cent CO₂. Some of the time the slag was a little sticky and did not flow very freely, but it was tapped off regularly once an hour throughout the test, and at no time did it cause any serious difficulty. About 20 lbs. of coke was consumed per square foot of fuel-bed area per hour, and to each 100 lbs. of coke 15 lbs. of limestone was charged. The air blast was preheated to about 440 F.; no steam was used. At the end of the test there was a layer of hard, flintlike clinker 4 to 6 ins. thick in the bottom of the producer.

A run with 15 lbs. of limestone per 100 lbs. of coke lasted more than 100 hours and gave satisfactory results. The air blast was preheated and steam was used. The slag flowed readily throughout the run, and at the close of the test the producer was found to be comparatively clean and clear from clinker.

Other runs of 100 hours' duration have been made, with and without preheated-air blast, with and without steam, and in each case little difficulty was experienced in tapping off the slag.

With preheated-air blast a more fluid slag is generally obtained, and the indications are that higher rates of combustion can be maintained.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR IN- STITUTE OF TECHNOLOGY.

The Determination of Phosphorus or Phosphoric Anhydride.

Phosphorus is highly important from the analytical standpoint. Its correct determination in soils, phosphate rock and prepared fertilizers is necessary for the evaluation of the material. Its percentage in iron ore and in iron and steel must also be known accurately, phosphorus being one of the two elements most injurious to iron products. Its determination in phosphor-bronzes is also important.

There are a variety of methods in use for the phosphorus determination in different materials, but practically all of them, whether for the large percentages of phosphoric acid present in phosphate rock, or the minute quantities in iron ore, are founded upon one principal operation, i. e., the separation of phosphorus from all the other constituents of the material by precipitation with ammonium molybdate.

The further treatment of the ammonium phosphomolybdate precipitate, whereby the quantity of phosphorus is determined may be by a number of different methods. The more important of these methods are the following:

(1) The direct weighing of ammonium phosphomolybdate and calculation of its phosphorus or P_2O_5 content.

(2) The solution of phosphomolybdate in ammonia, the precipitation of $Mg NH_4 PO_4$ by magnesia mixture and the subsequent weighing of phosphorus as $Mg_2 P_2 O_7$.

(3) The solution of the "yellow precipitate" in standard alkali, and the titrating of the excess of alkali by standard acid.

The second method is very largely used, and yields accurate results under careful manipulation. It is, however, very slow, and is subject to the fundamental errors which are always present when $Mg NH_4 PO_4$ is precipitated, i. e., the solubility of the precipitate and the difficulty of obtaining it of correct composition.

The direct weighing of ammonium phosphomolybdate is good when conditions of precipitation and drying are closely adhered to. The precipitate is not of perfectly constant composition, but since its phosphorus content is only about 1.6 per cent of the whole, slight variations in composition may be insignificant.

The third method, the so-called acid-alkali titration method, seems to be most generally useful of the

three for routine and commercial work, for it gives reliable results in a shorter time than is required by either of the other processes.

P_2O_5 in Fertilizers.

Preparation of Solutions.—For the titration of the purified yellow precipitate, a sodium hydroxide solution of about N/3 strength (about 14 grams per litre) is most convenient. One c.c. of this corresponds to about 0.001 gm. phosphorus pentoxide. A nitric acid solution exactly equivalent in strength to the alkali is used in back titration, phenolphthalein being employed as indicator for all titrations. The standardization of these solutions is as follows: Ammonium phosphomolybdate is prepared by adding a large excess (75 c.c.) of hot ammonium molybdate solution (30 gms. per l.) to a hot solution containing 0.5 gm. of $Na_2 HPO_4$ and 5-10 gms. of ammonium nitrate, the whole being acid with nitric acid. This should be done in a 500 c.c. Erlenmeyer flask, and the flask stoppered and shaken vigorously for five minutes after the addition of molybdate solution, when the precipitate is allowed to settle for fifteen minutes, and filtered on a hardened paper. Then it is washed with 1 per cent nitric acid and finally with 1 per cent KNO_3 until 3-4 drops of it fail to decolorize a drop of phenolphthalein solution, 50 c.c. of which had previously been made just alkaline with N/10 NaOH. The pure precipitate so obtained is then washed once with alcohol and dried at $100^\circ C$.

This precipitate has, very nearly, the composition $3(NH_4)_2 O \cdot P_2 O_5 \cdot 24MoO_3$, and contains 1.63 per cent P or 3.75 per cent $P_2 O_5$.

Portions of 0.4 gm. of precipitate are weighed out, dissolved in an excess of the NaOH solution, and the excess determined by back titration with HNO_3 .

$$\frac{\text{wt. of p. pt.} \times 0.0375}{\text{net vol. of NaOH}} = \frac{P_2 O_5 \text{ standard}}{\text{about 0.001 gm.}}$$

This standardization gives good results. The standard may be calculated direct from the ratio between the phosphomolybdate and the NaOH in their reaction, 1 $P_2 O_5$ being equivalent to 46 NaOH, or, best of all, the solution may be standardized against a fertilizer or phosphate rock sample of accurately known phosphorus content.

The Determination.

For fertilizers containing in the neighborhood of 12 per cent $P_2 O_5$, one gram samples are used. Their decomposition must be carried on so that organic matter is completely eliminated. To this end, 25 c.c. of

conc. HNO_3 and 5-8 c.c. of conc. HCl are added and the whole boiled down nearly to dryness, when 10 c.c. more of nitric acid are added and the evaporation continued to dryness over the water bath. The dry residue is baked for an hour at $110-120^\circ$, taken up in 10 c.c. nitric acid and 50 of water, filtered into a 250 c.c. volumetric flask and washed free of calcium salts. This treatment eliminates organic matter and silicic acid, both of which interfere with the precipitation of ammonium phospho-molybdate. The filtrate, after cooling, is made up to exactly 250 c.c. and several 25 c.c. portions each representing 0.1 gm. of sample are taken for precipitation. To the solution, ammonia is added until the precipitate of $\text{Ca}_3(\text{PO}_4)_2$ fails to re-dissolve, and then 10 c.c. of nitric acid, and the solution heated nearly to boiling; 20 c.c. of hot ammonium molybdate solution is now added slowly with constant stirring. The whole is shaken for five minutes, allowed to stand fifteen, and the clear liquid poured through a filter. The precipitate in the flask is washed once by decantation with 1 per cent HNO_3 , and then re-dissolved in 10 c.c. of 1:3 ammonia poured through the filter. The solution is heated a few c.c. of molybdate and double the bulk of water added, and the phospho-molybdate reprecipitated by the slow addition of 25 c.c. of hot 1:3 HNO_3 .

This precipitate, after shaking and standing as before, is filtered on a small paper, washed with 1 per cent HNO_3 and then with 1 per cent KNO_3 until the washings are neutral, when it is transferred, paper and all, to an Erlenmeyer flask, 40 c.c. of standard NaOH added, and the excess titrated with standard HNO_3 .

$$\frac{\text{Net NaOH} \times \text{P}_2 \text{O}_5 \text{ st'd}}{\text{O.1 wt. of sample}} \times 100 = \% \text{ P}_2 \text{O}_5$$

When the substance for analysis is phosphate rock, the treatment with aqua regia may be omitted, 10 c.c. of nitric acid being used in its stead. It is advisable, however, to evaporate and dehydrate twice in order to make the separation of silica complete.

The weight of the sample taken should be governed by the approximate percentage of phosphorus present.

The Gravimetric Methods.

The phospho-molybdate precipitate obtained by the method outlined above, is freed from acid and dehydrated by long heating at $150-170^\circ \text{C.}$, going to the definite compound $(\text{NH}_4)_3 \text{PO}_4 \cdot 12 \text{MoO}_3$.

The precipitate is filtered upon a weighed Gooch crucible, washed with nitric acid and dilute ammonium nitrate, and dried to constant weight at 160°C. in a current of air if possible, and weighed.

$$\text{Weight ppt.} \times 0.0375 = \text{wt. P}_2 \text{O}_5$$

The determination of phosphorus in iron ore has previously been described in a former article of the present series (this journal, Vol. 15, No. 5). Its determination in iron and steel and in non-ferrous alloys will be described in a later issue.

DETERMINING THE SODA IN "BLACK LIQUOR."*

By EDWIN SUTERMEISTER and HAROLD R. RAFSKY.†

In the manufacture of cellulose by the soda process wood is digested under pressure with a solution of sodium hydroxide. The liquid separated from the resulting pulp is called "black liquor," and contains the sodium hydroxide unconsumed in the reaction, together with the sodium salts of acids formed by the decomposition of the wood. A precise evaluation of this residual sodium hydroxide would give valuable information on the exact consumption of caustic soda by wood, and perhaps help to explain the chemistry of the digestion process.

The method now employed is simply one of titration with acid, using a solution of phenolphthalein as an outside indicator. In detail: 25 cc. of black liquor are diluted with 300 cc. of water; 10 cc. of a concentrated BaCl_2 solution (400 grams to liter) are added to precipitate carbonates and the organic acid radicles which yield insoluble barium salts, and the solution is titrated with N acid (HCl , HNO_3 or H_2SO_4). The end point is determined by removing drops of the solution at intervals during the titration and allowing them to fall gently from a stirring-rod into a solution of phenolphthalein in water just covering the bottom of a beaker. When a drop fails to develop a red color in the indicator solution immediately surrounding it, the end point is considered to be reached. This method is approximate only, but checks within 5 per cent can generally be obtained—*e. g.*, three successive titrations required respectively 5.00, 4.90, 5.11 cc. N acid.

The difficulties in arriving at the end point are: First, the distinguishing of the red color of the indicator from the brown of the drop; and, second, the slow development of the red color around the drop. The real trouble, however—dependent, perhaps, on the two just mentioned—is that the end point recorded varies with the working conditions. Thus if the titration is carried out at dilutions other than the one given above, widely differing values are obtained, as is shown in the following table which gives the results of titrating 25 cc. of black liquor at different dilutions:

Total vol. of diluted black liquor.	Individual titrations. <i>N</i> acid.	Average.
39 cc.	3.50 cc. }	
	3.42 cc. }	3.46 cc.
88 cc.	3.67 cc. }	
	3.60 cc. }	3.63 cc.
185 cc.	3.56 cc. }	
	3.70 cc. }	3.62 cc.
	3.60 cc. }	
435 cc.	4.13 cc. }	
	4.62 cc. }	4.45 cc.
	4.30 cc. }	
	4.74 cc. }	
835 cc.	5.00 cc. }	
	4.90 cc. }	5.00 cc.
	5.11 cc. }	

*From the Journal of Industrial and Engineering Chemistry.
†Chemical Laboratories of S. D. Warren & Co., Cumberland Mills, Maine.

1.635 cc. 4.92 cc. }
 5.15 cc. } 5.03 cc.

Again, if there is added to a black liquor (which has been analyzed by the present method) a known amount of NaOH and this "fortified" black liquor is then titrated, the increase of acid used in titration is smaller than the amount equivalent to the NaOH added. For instance: To a black liquor titrating 6.39 cc. acid, NaOH was added equivalent to 8.28 cc. acid, and duplicate titrations of this "fortified" black liquor showed readings of 13.54 and 13.64 cc., an average of 13.59 cc., while the calculated result is 14.67 cc.

One possible explanation of these inconsistencies is that the OH ions are absorbed by the colloids present. Another theory supposes the presence of an organic complex which combines with OH ions, the resulting molecule having but a small dissociation constant. On increasing the concentration of OH ions (as in a "fortified" black liquor) the dissociation is checked, whereas a decrease in the concentration of OH ions (as in dilution) increases the dissociation and hence the total amount of OH ions present.

The following is a description of numerous attempts to improve our original method, and is published in the hope of bringing forth some more successful method, or of starting a discussion and stimulating further work along this line.

Preliminary Experiments.—Small test tubes, partly filled with a solution of phenolphthalein in water, were tried for the examination of the individual test drops, but no satisfactory end point was obtainable. The idea of using phenolphthalein directly in the solution to be titrated after the addition of a white substance such as BaSO₄ or china clay to lighten the color, proved a failure as the color change was gradual and indefinite.

Elimination of Precipitate.—We next sought to eliminate the voluminous precipitate produced on addition of BaCl₂, in order to obtain a clear liquid for titration. Ordinary settling, filtration, and centrifugal filtration proved unsatisfactory, but in a Babcock centrifuge a clear orange colored solution was secured by adding clay to the regular titration mixture and centrifuging for 7 or 8 minutes. This clear liquid when poured off and titrated with phenolphthalein directly did not give very close duplicates—*e. g.*, 13.76 and 14.64 cc. N/10 HCl.

Indicators Tried.—As we were unable to decolorize the clear centrifuged solution with charcoal, we directed our attention to procuring a better indicator. Litmus, Congo red, and lacmoid, with blue-red or red-blue color change were unavailable as the orange color of the solution interfered with the end point. A mixture of dyes, the color of which was practically complementary to the orange shade, was added in an attempt to produce a gray—so that an indicator could be used to better advantage—but the dyes changed color, owing to the action of the alkaline solution, and satisfactory results were not obtained. A mixture of phenolphthalein and malachite green showed some

promise but was finally discarded, as the malachite green when used in sufficient amount to cover the orange color tended both to precipitate in neutral solution and to mask the last traces of the red of the phenolphthalein. We found, however, that by using an *excess* of phenolphthalein alone we arrived at a satisfactory and definite end point. Our method was to add a few drops of indicator, titrate to disappearance of red, add a large excess of indicator, and again titrate to the disappearance of red, repeating this operation till no red color developed on addition of more indicator.

Determination of Ratio.—Up to this point we were titrating a portion of the clear liquid obtained by precipitating the black liquor with BaCl₂ and centrifuging. It now became necessary to determine the ratio of the NaOH in the portion used to that in the entire volume of clear liquor and precipitate.

The first method attempted was to find the total amount of NaOH present in the entire mixture (20 cc. BaCl₂, 50 cc. black liquor, 20 grams clay, and 175 cc. of water) by titrating the entire quantity of centrifuged liquor in the usual way and then repeatedly extracting the sludge with water, and centrifuging till the final extraction gave no test with phenolphthalein. As the total volume of the solution was too large to work with conveniently, one-fifth was taken. This idea worked well until the third extraction with water, when the clay did not drag down the sludge, but left it in suspension, making titration impossible. Addition of more clay was of no avail, and consequently as the sludge reacted strongly alkaline, the method was abandoned.

The problem was next attacked on the theory that if a known amount of NaOH were added to a black liquor and the mixture centrifuged as usual, the same percentage of the added NaOH as of that originally present would be found in the clear liquor. Having determined what percentage of the added NaOH was present in the centrifuged liquor titrated we could then calculate the total amount of NaOH present in the original sample of black liquor.

With this basic idea, we made up the following two mixtures: 25 cc. of black liquor, 10 grams of clay, and 50 cc. of BaCl₂; and 25 cc. of black liquor, 10 grams of clay, 45 cc. of BaCl₂ and 5 cc. NaOH (= 48.80 cc. N/5 HCl). These were centrifuged under the same conditions and 10 cc. of each of the centrifuged liquors titrated. The first titration (2.12 cc. N/5 HCl) representing the amount of NaOH present from the black liquor; the second (8.80 cc. N/5 HCl) the amount of NaOH present from the black liquor plus added NaOH. Thus the added NaOH present in the 10 cc. of centrifuged liquor = 8.80 — 2.12 = 6.68 cc. N/5 HCl. The percentage of the total added NaOH present in the 10 cc. of centrifuged liquor = 6.68 — = 13.7 per cent. 48.80

According to the above theory only 13.7 per cent of the NaOH present in the original black liquor is to be found in 10 cc. of the clear centrifuged liquor and as this 13.7 per cent is represented by 2.12 cc. *N*/5 acid the total amount of NaOH present would be equivalent to 15.48 cc. *N*/5 or 3.09 cc. *N* acid. A series of similar tests were made of which the following is a summary: Two determinations of pure black liquor, carried out in the manner outlined above, gave as titrations for 10 cc. of the centrifuged liquor 2.14, 2.10, and 2.19, 2.14, 2.12 cc. *N*/5 acid; average, 2.14 cc. *N*/5 HCl. The table below gives the results of four tests on "fortified" black liquors, *i. e.*, black liquors to which NaOH has been added. All figures given, except the last column, indicate *N*/5 acid used.

The average of the four values found below is 3.14 cc. *N* HCl for the titer of 25 cc. of black liquor. The peculiar part, however, for which we can assign no reason is: That by titrating according to our original method we get a value of from 6-7 cc. *N* acid for the titer of the same volume of black liquor. Until we can explain why this discrepancy occurs, we cannot proceed further with this method.

TABLE I.

	Titration 10 cc. centrifuged fortified black liquor.	Value of NaOH present from black liquor.	Value of NaOH present from added NaOH (I-II).	Value of total NaOH added.	Per cent total added NaOH present in 10 cc. centrifuged liquor (III) (IV).	Calculated value of NaOH in original black liquor $\left[\frac{(II)}{(IV)} \times 100 \right]$	NaOH value of original black liquor in terms of <i>N</i> acid.
1 ..	8.82 8.79 8.71	2.14	6.66	48.80	13.65	15.68	3.14
2 ..	8.67 8.67 15.45	2.14	6.55	48.80	13.42	15.94	3.19
3 ..	15.45 22.55	2.14	13.31	97.60	13.63	15.70	3.14
4 ..	22.54	2.14	20.40	146.40	13.92	15.37	3.07

Average—3.14 cc. *N* acid.

In the above series of determination we centrifuged the mixture 12 minutes, poured off equal quantities of clear liquor, and centrifuged again for 3 minutes, which left a perfectly clear liquid for titration.

Electrometric Method.—A problem very similar to the one at hand, *i. e.*, the determination of the acidity of tan liquors, has reached a successful solution by the employment of the electrometric method of titration, as reported by Sand and Law¹ and by Sand, Law and Wood.² They measure the voltage of a cell, one arm of which is a normal calomel electrode, and the other a hydrogen electrode dipping into the tan liquor to be titrated. Acid is added to the tan liquor until a potential of 0.69 volt is registered, which indicates neutrality.

Through the kindness of Dr. Geo. S. Forbes, of Harvard University, one of the writers was permitted

to use apparatus and space in his laboratory to test out this method. We are also indebted to Dr. Forbes for much valuable advice and assistance. The work reported below was carried out very roughly, the object being merely to test the applicability of the method for our use. Our apparatus consisted of a cell similar to that employed in the tan liquor determination, the potential of which was measured by the compensation method, using a potentiometer box. We employed a D'Arsonval galvanometer and although this tended to polarize the hydrogen electrode, for approximate work it proved more convenient than an electrometer.

As we were uncertain as to the magnitude of a possible reducing action of black liquor on the hydrogen electrode, we could not assume that the potential corresponding to a given concentration of a pure NaOH solution would necessarily indicate the same concentration of NaOH in the black liquor solution. To test this point we titrated a black liquor according to our original method to get the approximate concentration of NaOH; then we made up a pure NaOH solution of similar concentration (0.026 *N*), and read off the potentials of the two solutions in the cell.

Calculated potential	1.00 volt
Black liquor	0.97-0.98 volt
Alkali	0.99 volt

The above potential in the alkali, and especially in the case of the black liquor, was not reached for several minutes.

Another determination of a solution one-tenth as strong, 0.0026 *N*, gave a voltage of 0.91 in the black liquor. The calculated voltage is 0.94.

Both the above determinations indicated that the reducing action of the black liquor did not greatly affect the hydrogen electrode in alkaline solution, so we next tried the direct titration of the black liquor.

For this purpose we took 25 cc. black liquor, 10 cc. BaCl₂ (400 grams to liter), and 220 cc. water. A similar mixture by our old method titrated 13.1 cc. *N*/2 acid. The first titration registered no sudden fall of potential but rather a steady diminution of voltage up to 28.6 cc. acid (as much as was added) and a second trial resulted similarly. When, however, about 10 cc. concentrated HCl was added, the colloids coagulated and the voltage dropped to 0.33.

To make certain that the H electrode had not been affected by its immersion in the black liquor, immediately after the above titration it was placed in a neutral KCl solution and the voltage found to be above 0.6 volt. In contrast with the black liquor titration above, at the neutral point in the titration of an NaOH solution, as indicated by phenolphthalein, the addition of an extra quarter cc. of *N*/2 acid causes a very sharp diminution of the potential of the cell. From the determinations given above we concluded that the electrometric method was, as applied, inapplicable in our case.

SUMMARY.

The present method for the determination of NaOH

¹J. Soc. Chem., Ind., 30, 1, 2.

²Ibid., 30, 14, 872.

content of black liquors is one of titration with acid, using phenolphthalein as an outside indicator.

In the attempt to improve this method, the more important ideas worked upon were:

1. The elimination by centrifugal action of the precipitate formed by BaCl_2 and the subsequent titration of the clear liquor.
2. The use of various indicators, and the successful method of employing phenolphthalein.
3. The determination of a ratio between the centrifuged liquor and the sample of black liquor taken
4. Electrometric method.

None of the methods or modifications thus far tested has proved entirely satisfactory, and the original method, although it gives only approximate results, is the best one at present available.

IODOMETRIC COPPER TITRATIONS.*

By K. SUGIURA and P. A. KOBER.

In studying a large number of copper salts of amino acids,¹ we obtained the copper as a hydroxide or oxide by precipitating with alkali under suitable conditions. After washing the precipitate on the filter paper and the flask thoroughly, we transferred the paper with precipitate back into the flask and dissolved with 20-25 cc. of 10 per cent acetic acid. The resulting copper acetate was then titrated with potassium iodide and sodium thiosulfate solution in the usual manner, using starch solution, finally, as an indicator. It was noticed that these solutions *did not show a return* of the usual *blue color of starch* produced in these reactions, or, in other words, showed a *stable end point*; while those titrations made in the presence of nitrates gave too high results and showed an *unstable end point*.

Recently Kendall² described a technic designed to remove the nitrates, based on the use of phenol under certain conditions. According to Kendall, his method is quick and when suitably controlled gives satisfactory and accurate values. In a later article Kendall³ points out a source of error. We hope to show that the precipitation with alkali and solution with acetic acid will accomplish the same end, is simple, and accurate, removing all unnecessary and interfering substances from the copper solution.

EXPERIMENTAL.

As a standard solution, we employed a 0.04 *M* copper nitrate solution, made from cupric oxide,⁴ standardized many times by the electrolytic method.

The standardized 0.04 *M* copper nitrate solution is made by dissolving 3.184 g. of copper oxide in dilute nitric acid. After evaporating almost to dryness, to remove the excess of nitric acid, the copper nitrate

solution was diluted and made up to one liter. To standardize this solution, we took 50 cc.⁵ of 0.04 *M* copper nitrate solution at 18°, in a platinum dish,⁶ added 2 cc. of concentrated nitric acid, 3 cc. of 95 per cent alcohol and brought the volume with water within $\frac{1}{4}$ in. of the edge of the platinum dish. Electric current of 0.8-1.2 amperes was then passed through the solution for about 6 hours. The end of electrolysis was shown by testing a small portion of the solution with hydrogen sulphide. When the electrolysis was finished the dish was inclined and the nitric acid diluted and displaced by a stream of cold water from a wash bottle. The electrodes were removed and the dish was washed once more with water and the water finally removed from the platinum dish with 95 per cent alcohol. The dish was then dried in an oven at a temperature of 70°-90° for 5 minutes and in a vacuum desiccator for about two hours, after which it was weighed.

A few examples will suffice:

Solution No.	0.04 <i>M</i> $\text{Cu}(\text{NO}_3)_2$ taken cc.	Copper found by electrolysis.	Equivalent in CuO .	Theoretical amt. of CuO for 0.04 <i>M</i> $\text{Cu}(\text{NO}_3)_2$	Factor.
1	50	0.1263	0.1581	0.1592	0.993
1	50	0.1263	0.1581	0.1592	0.993
1	50	0.1264	0.1582	0.1592	0.994
Average,	50	0.1263	0.1581	0.1592	0.9933
2	50	0.1261	0.1578	0.1592	0.991
2	50	0.1260	0.1577	0.1592	0.990
2	50	0.1261	0.1578	0.1592	0.991
Average,	50	0.1261	0.1578	0.1592	0.9906

These results show that the cupric oxide is somewhat impure. In order to actually prove this we electrolyzed, dried and weighed portions of cupric oxide, which gave the following results:

Sample No.	CuO taken. Grams.	Cu found by electrolysis. Grams.	Equivalent in CuO . Grams.	CuO found. Per cent.	Impurity. Per cent.
1	0.2539	0.2000	0.2503	98.58	1.42
2	1.6095	1.2672	1.5859	98.53	1.47
3	1.6095	1.2671	1.5858	98.53	1.47
4	1.6095	1.2670	1.5857	98.52	1.48

To determine the factor of the 0.04 *N* sodium thiosulfate 50 cc. of standard copper nitrate solution were diluted to 100-150 cc. After adding 2-3 drops of 1 per cent phenolphthalein indicator, 33 per cent alkali was added drop by drop until a slight precipitate of copper hydroxide remained undissolved. The solution was then titrated with 0.2 *N* carbonate-free sodium hydroxide⁸ (containing $\text{Ba}(\text{OH})_2$) until a change of color was observed. The solution, after settling, was filtered through good Swedish filter paper, and the precipitate and precipitating flask washed three or four times with a little water. The precipitate with filter paper was then transferred back into the flask and the

*From the Journal American Chemical Society.
¹Kober (Preliminary Communication), J. Biol. Chem., 10, 9 (1911).

²Kendall, this Journal, 33, 1947.

³Kendall, *Ibid.*, 34, 317.

⁴Elmer and Amend's tested purity product.

⁵Carefully standardized flasks, pipets, burets and weights were used in this investigation.

⁶The platinum dish weighed about 50 g.

⁷The determinations recorded in this paper were made during the course of a year, along with other work. Therefore, many different solutions were used, and obviously, the solutions have not always the same factor.

⁸An excess of alkali containing carbonate will of course keep some of the copper in solution as a carbonate complex, but under the conditions given above this is impossible.

copper hydroxide dissolved in 20-25 cc. of 10 per cent acetic acid (warming the solution, if necessary). After adding 2-4 g. of potassium iodide to the colled solution, sodium thiosulfate was added slowly until most of the iodine had disappeared. Then a little fresh starch solution and more thiosulfate solution were added until the blue starch color was discharged. The end point under these conditions was sharp and stable. As many controls showed, the filter paper had no influence on the results.

A few examples of titration follow:

0.04 M $\text{Cu}(\text{NO}_3)_2$ taken, cc.	Weight of copper found after electrolysis, Gram.	Dissolved in HNO ₃ , precipitated with NaOH, etc., titrated with 0.04 N $\text{Na}_2\text{S}_2\text{O}_3$, cc.	Titred directly, without electrolysis (precipitation method), cc.
25	0.1261	48.93	..
50	0.1260	48.88	..
50	0.1261	49.03	..
50		..	48.99
50		..	49.00
50		..	49.00
50		..	48.98
50		..	48.90
Av. 50	0.12607	48.95	48.97

The thiosulphate solution was kept in a dark bottle, provided with a soda lime and calcium chloride tube. In a shaded place and at room temperatures the solution changed its strength, but slowly, as the following table shows:

Dates, March	11	12	13	14	15	16	17
Factor....	0.9972	0.9969	0.9965	0.9959	0.9953	0.9943	0.9925

Even large amounts of nitric acid, or of any other mineral acid present in copper solutions, do not interfere with the iodometric titrations if the acid is neutralized with alkali and the copper hydroxide is filtered off and redissolved with acetic acid as described above. This is shown below:

Solution No.	0.04 M $\text{Cu}(\text{NO}_3)_2$ taken, cc.	Added HNO ₃ (conc.), cc.	Titred by 0.04 N $\text{Na}_2\text{S}_2\text{O}_3$, cc.
1	25	0.0	25.00
1	25	0.5	25.00
1	25	1.0	25.00
1	25	2.0	24.99
1	25	3.0	24.97
1	25	4.0	25.02
1	25	5.0	25.00
Average, 25			24.997

*Blank tests on the reagents were made from time to time, and corrections applied when necessary.

Solution No.	0.04 M $\text{Cu}(\text{NO}_3)_2$ taken, cc.	Acid added, cc.	Titred by 0.04 N $\text{Na}_2\text{S}_2\text{O}_3$, cc.
2	25	None	24.58
2	25	None	24.58
2	25	10 cc. HNO ₃	24.56
2	25	10 cc. HNO ₃	24.58
2	25	10 cc. HCl	24.57
2	25	10 cc. HCl	24.58
Average, 25 cc.=	24.77, 0.04 M		24.578=24.77, 0.04 N

The results show clearly that the amount and nature of the acid had no influence on the determination, when the copper was carefully removed as a hydroxide. That the flocculent hydrate or hydrogel may absorb a small amount of nitrate is very probable; but that the error of such an amount is small, and entirely negligible, is

apparent from the results just given. The stability¹⁰ of the end-point indicates the same conclusion.

In order to see if copper in the form of copper sulfide could be treated in the same manner and with the same accuracy, the following experiments were made:

To 25 cc. of 0.04 M copper nitrate solution neutralized with alkali in a 250 cc. beaker, 2 cc. concentrated nitric acid were added and diluted to 50-100 cc. with water. After heating to 90°-95° hydrogen sulfide was passed slowly through the solution until the precipitation was complete. The solution was then filtered through a Gooch crucible, using a very fine asbestos mat.¹¹ To insure complete precipitation the filtrate was again treated with hydrogen sulfide, and filtered if necessary. After washing the precipitate and beaker several times with a little water, the Gooch crucible¹² with the copper sulfide was placed back in the same beaker and dissolved with strong nitric acid or aqua regia. This was accomplished by placing the beaker on the steam bath for 2-3 hours. After filtering off the sulphur and asbestos carefully the copper was precipitated as described above and titrated:

0.04 M $\text{Cu}(\text{NO}_3)_2$ taken, cc.	Titration from CuS with 0.04 N $\text{Na}_2\text{S}_2\text{O}_3$, cc.	Titration from controls, cc.
25	24.98	25.03
25	24.97	25.00
25	25.04	25.06
25	25.07	25.05
25	24.84	24.83
25	24.85	24.83
Average, 24.96		24.97

Considering the number of manipulations and the error of buret reading, etc., the results can be considered satisfactory.

The smooth writing qualities possessed by gold fountain pens may be attributed to the tiny bit of white metal—iridium—fastened to the tip of the pen. Iridium is an exceedingly rare metal, according to the United States Geological Survey, not more than 5,000 ounces being produced each year, of which perhaps about 500 ounces are recovered in the United States, mostly from imported platinum sand and from copper ores and bullion. The price demanded for iridium has been increasing rapidly, and in 1911 it ranged from \$60 to \$64 an ounce for pure metal. Owing to its unique qualities, iridium finds a fairly extensive use. Most of the metal produced is probably used for hardening platinum. It is further used for various scientific and technical purposes, such as standard weights, pivots, contact points, and as previously stated, for gold-pen points. Iridium black, an oxide of the metal, is highly valued as a pigment for decorating chinaware. According to the Bureau of Statistics, 3,905 troy ounces of "iridium and iridium in native combination with platinum metals," valued at \$210,616, were imported into the United States in 1911.

¹⁰Kober, Am. Chem. J., 41, 430 (1909).

¹²Filter paper cannot be used, instead of asbestos, as its hydrolytic products with mineral acids prevent the precipitation of copper hydroxide on neutralization.

SCIENTIFIC CELLULOSE INVESTIGATION.*

By C. F. CROSS, B. SC., F. I. C.

In Paper for April 17, 1912, the suggestion of C. F. Cross for the adoption of a definite standard or normal measure of cellulose was discussed. It was noted that the term "cellulose" is conceived and applied very variably in scientific investigations and writings, and the need of precise definition was emphasized. In a later communication to The Chemical World, Mr. Cross returns to the subject, taking as his text a series of articles in the *Zeits. Farben, Ind.*, 1911-12, on the "Estimation of Cellulose in Woods and Textile Fibers," in which the authors, J. König and F. Hühn, seek to maintain a position which Mr. Cross deems far removed from what is generally accepted. In his later paper Mr. Cross says it evidently is necessary to insist upon fundamental points and clear definitions in this region, and continues: It is clear that methods of estimating cellulose and the critical evaluation of such methods, briefly summarize our fundamental knowledge.

Now, all our investigations issue in two main conclusions in respect of cellulose. Cellulose is only known to us as a residue of processes of "purification" of fibers or cellular raw material; and as these processes are not without action on the cellulose, the residue is of necessity a variable, varying with the process and the conditions and intensity of action.

It is, therefore, incorrect to speak of the estimation of cellulose as we should of, say, silica in a complex silicate. The analyst does not concern himself with the phases of silica in the process of its separation from a mixture; it is sufficient that it is isolated and finally ignited to be weighed as SiO_2 .

In the isolation of cellulose we proceed by way of systematic exhaustion: (a) by neutral solvents, *e. g.*, ether, alcohol, water; (b) by simple hydrolytic agents, mainly alkaline, treatments of this group being carefully regulated to produce the minimum of change in the cellulose.

Thus exhausted, the residue is a possible mixture of cellulose, ligno-cellulose and cuto-celluloses. In the majority of cases the latter are present in insignificant proportions. The major problem in a process of cellulose estimation is the elimination of lignone constituents, and it is this problem which has been the main subject of the investigations of König and Hühn.

These investigations have covered the range of processes identified with the names of Henneberg (Crude fiber, "Rohfaser"), König, H. Müller, Cross and Bevan, Schulze, Tollens, and others. A similar comparative study has been recently made by M. Renker (*Inaug. Diss.*, 1909, Berlin), with the result of confirming the general adoption of the process of chlorination. This investigation and its conclusions have been favorably received by specialists and tech-

nologists, and also endorsed by the International Commission, and it would be considered gratuitous to reopen the subject.

But König and Hühn are not influenced by this antecedent position. They consider that the chlorination method does *not* estimate, *i. e.*, isolate cellulose, but a complex of "true cellulose," hemihexosanes and pentosanes.

Their conclusion is evolved from the comparative study of the "König," process, the basis of which is a digestion of the cellulose material with a special acid eragent, glycerin-sulphuric acid, *i. e.*, a solution of 20 gm. H_2SO_4 in 1,000 cc. glycerin, the digestion being carried out at 137°C . Chemists will not need to be reminded that the typical cellulose cotton is profoundly attacked, and constitutionally modified under this treatment. The authors record that the product from cotton is a friable powder, representing 88 per cent of the weight of a cellulose isolated by the chlorine method. But it is a "true cellulose" freed from the "hemihexosanes" of the reputed "normal cellulose." And "plain" chemists will be interested to know how this unexpected judgment is justified.

Since all criteria based upon hitherto accepted principles must have failed, the authors have devised a further little scheme of verification of their own. Dissolving the product in the ZnCl_2HCl solvent, they observe the specific rotation which slowly develops to a maximum (2 to 3 days) as a result of hydrolysis, to again diminish, apparently as the result of inverse processes of condensation. Cellulose "purified" by the glycerin-sulphuric acid method is found to give the highest maxima, specimens isolated by the chlorination process give lower maxima, whence it is concluded that the König product and decomposition is the "true cellulose," and the accepted standards of normal cellulose are by comparison heterogeneous mixtures.

As a result of further critical discussion of this group of methods, the authors select, as next in order of distinction, a recently published method of Tollens and Dmochowski (*J. F. Landw.*, 58, 1, 1910), which consists in first obtaining the "rohfaser" residue of successive hydrolyses, acid and alkaline, and digesting this residue with strong nitric acid to eliminate unsaturated and oxidizable groups. The finally purified residue is weighed and the result is then subjected to a simple treatment of rehabilitation, being multiplied by the factor 1.1, the "corrected" figures showing quite respectable approximations to the yields of cellulose by standard methods.

It is really difficult to criticize these conclusions and proposals. One can only take the distinguished names of the chemists who father them as a guarantee that they are based on unexceptionable laboratory methods, and as studies of degradations of cellulose they have undoubted value.

In the preceding article in this journal (see Paper, April 17, 1912), the author dealt with the question of the "normal cellulose" and its definition. That defini-

*From Paper, July 17, 1912.

tion involves a threefold standard of convergent verifications—resistance to hydrolysis, resistance to oxidation and maintenance of structural integrity as expressed in terms of breaking strain and elasticity. We may now, with advantage, add a complementary standard of criticism upon which to meet and dispose of the suggestions of the authors whose work has been thus briefly described.

Cellulose, as a section of science, rests upon a tripod composed of the plant, that is the plant world: the factory, that is the manufacturing industries of which cellulose is the raw material; the laboratory, that is the pure chemical science of the subject.

The perception of these relations and the order of their interdependence may be a matter of intuition. It may be clear to the child or the philosopher, it certainly does not automatically rule, and adjust the perspective of the great "middle class," that is the class between these two more important sections of the family. If it did, we suggest, we could not be seriously asked to bring our estimations of cellulose into line with arbitrarily selected laboratory products of breakdown, undefined except by methods involving necessarily an almost unthinkable complexity of interactions.

Whatever we know of cellulose is conditioned by such stereoscopic view as we now obtain by observation in the directions of vision aforesaid. "Normal products" of the laboratory are normal when they further conform with the exigencies of manufacturing industry, and as industry in this case is only a development of economic botany or vegetable physiology, but on a lower plane, we have to compare our "industrial normal" with the "natural" normal products.

Such views are the working atmosphere of the school we claim to represent; we only become aware that these principles are not self-evident when we find ourselves in the presence of contributions such as those under discussion, written from an entirely divergent point of view and criticism.

Our opinion is that, as there is no question of difference as to experimental numbers, and the divergence is one of fundamental interpretation, there are psychological factors even of so impersonal an issue as "the normal cellulose," and the best method of estimating it.

In such a case, we appear to arrive at an *impasse* in which experimental numbers lose their significance, and it is, we think, therefore, opportune to formulate the general perspective of the methods thus attacked and leave the issue to our fellow students.

It may, perhaps, be useful to younger students to put on record a condensed bibliography of the main line of development of the new established practice in the analysis of cellulosic raw materials, as follows:

H. Müller, *Pflanzenfaser*, Leipzig, 1876. (Method of isolation of cellulose by Br. Aq.)

M. Vétillart. "Etudes sur les fibres vegetales textiles," Paris, 1876. (Quantitative estimation by microscope.)

Cross and Bevan. "The Chemistry of Bast Fibres" (*Jour. Chem. Soc.*, 41, 90, 1882). (Method of isolation of cellulose by chlorination.) Reports. Col. Ind. Exhibition, London, 1887. Article, "Miscellaneous Fibres." (Systematic analysis of vegetable raw materials.)

Dean and Tower. "Determination of Cellulose in Wood by the Chlorination Process." (*Jour. Amer. Chem. Soc.* 29, 1, 119, 1907). (Study of chlorination process in relation to more resistant lignocelluloses.)

M. Renker. "Ueber Bestimmungs Methoden der Cellulose." Berlin, 1909. (Dissertation). Comparative study of all known processes of estimating cellulose.

The largest known phosphate field in the world lies in the Rocky Mountain region in the States of Idaho, Montana, Utah, and Wyoming, and most of the deposits belong to the United States, being on public land. Phosphate rock, as is well known, is the principal source of phosphorus, one of the three necessary plant foods. The exact boundary of this phosphate-bearing area is still undetermined, but each year as investigation has been pushed by the United States Geological Survey its limits have been more accurately defined by extension in some directions and retraction in others. Phosphate in this general region was first discovered in northeastern Utah and southeastern Idaho in the vicinity of the Idaho-Utah-Wyoming state lines. From this locality the deposits have been traced north, southeast, and west halfway across the states of Idaho, Utah and Wyoming, and northward to the vicinity of Helena, in west-central Montana, until now the phosphate beds are known over an area extending approximately 220 miles in an east-west direction and 420 miles from north to south. Only a small part of this territory, of course, is underlain by phosphate deposits that are commercially valuable. In many places the phosphate beds, although present, occur at such great depths below the surface that they will probably never be mined; and in other parts of this complexly folded area the phosphate beds have been entirely removed by erosion. However, the tonnage of high-grade phosphate rock in this region is enormous, the estimates running up into the billions of tons. The rock phosphate itself can usually be recognized in the field by its oölitic texture—that is, by the fact that it is a mass of grains like small shot cemented together. The rock varies in color from coaly black—in some places it was originally mistaken for coal—to dull gray or iron stained. Most of the phosphate rock emits, when broken or struck, a fetid odor, which is supposed to be characteristic of these minerals. Its "float" is characteristically marked with a thin film of bluish-white bonelike coating, resembling chalcedony. This coating is useful in tracing the concealed outcrop in the field by means of scattered fragments to be found in the overlying soil.

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NOTES AND COMMENTS.

Latest Achievements and Problems of the Chemical Industry.

The general lecture delivered by Dr. Carl Duisberg of Elberfeld, Germany, before the International Congress of Applied Chemistry in New York on Sept. 9 last is inspiring reading for the industrial chemist.

"The Latest Achievements and Problems of the Chemical Industry" was his subject, and so well was that big subject followed in his hour's address, that the chemist who is so occupied with his own line of endeavor as to lose touch with much of the progress in other fields, will find in it much to interest and inspire him.

Dr. Duisberg said in introduction: "Probably in no domain of human knowledge and endeavor have the combined forces of theory and practice, intimately acting and reacting upon each other, made such immense strides and lead to the solution of such difficult problems as in the chemical industry, an industry which indeed had its beginning in the distant past, but in its vast development and international character is essentially a child of modern times. Success has so emboldened this industry that it considers itself capable of solving any problem, provided the men in its service are well trained in theory and practice and ready to

devote themselves to the best of their ability, with patience and perseverance, to the object in view. . . ."

The production of power and of cold, the size of apparatus, materials, iron alloys, sulphuric acid, ammonium sulphate, nitrogen compounds, soda and chlorine, tin, reducing and oxidizing agents, peroxides, rare metals, and artificial gems are the headings under the subject of inorganic chemistry "which is taking a more and more important position beside organic chemistry."

Under Applied Organic Chemistry are discussed: Coal tar hydrocarbons, intermediate products, coal tar colors, pharmaceutical chemistry, chemotherapy, synthetic perfumes, acetylcellulose, non-inflammable celluloid and finally synthetic rubber.

The great field of the organic chemical industry, founded, as it is, upon pure scientific research, belongs almost wholly to Germany. Much of the progress made in inorganic chemistry, similarly founded, is German. America stands high in the ingenious application of principles, in the creation of appliances, in inventiveness. The alliance between the forces of theory and practice in American chemistry lacks strength. These are some conclusions forced upon one by Dr. Duisberg, and they add emphasis to the questions which have been agitating American chemists, and about which, of late, so much has been spoken and written: "How can American industrial research be stimulated and improved?" and "How can we improve the training of industrial chemists and chemical engineers?"

Many answers to these questions have been put forward and plans suggested. Results will come gradually, not suddenly, through big endowments of laboratories, but gradually through the education of the general public and particularly of the leaders of the industries, to an appreciation of what the chemist has done for the industries, and therefore what he can do. The Eighth International Congress of Applied Chemistry should be a great agent for public education of just that sort.

Synthetic Rubber.

The value of the annual product of American rubber factories alone is \$220,000,000. In this production \$100,000,000 worth of crude rubber is consumed. These facts, alone, would account for the prominent position synthetic rubber occupies in the attention of the chemical world in general, and the rubber industries in particular.

The story of the synthesis of indigo is being repeated. The production of synthetic rubber, by several distinct methods, has already been achieved on a laboratory and even a small factory scale. Beginning with the production of rubber from isoprene by Bouchardat in 1879 and continuing through the work of Tilden, Gladziatzky, v. Wittorf, Euler, Harries, Hofmann and others, the problem has been gradually unfolded.

It is interesting to note that a method entirely dif-

ferent from the isoprene and turpentine methods of the above workers has recently been announced by Professor Perkins. In this method the source is starch, which is caused to ferment in such a way as to produce large quantities of butyl and amyl alcohols. These materials form the starting points in the new English process. According to Perkins, synthetic rubber can be produced very cheaply by this method.

But whether it can or not, the actual manufacturing of synthetic rubber is already foretold. It may have been produced up to the present time in but small amount; it may have been inferior to the natural rubbers in its properties; the technical problems of manufacture may yet have to be solved; even new processes and sources may have to be discovered, but the prize is too rich from a financial view point alone. The problem is opening up, slowly, gradually. It is a difficult one, a problem that enters the field of colloids, but it would be a rash individual indeed, who would say that synthetic rubber will never be a commercial success.

B. B. FREUD.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, Washington D. C.:

- 1,030,909. Composition of Matter for **Fire-Proofing** and Other Purposes. Giuseppe Antonio Mesturino, Turin, Italy. Patented July 2, 1912.
- 1,030,972. Process for **Direct Nickeling** of Aluminum or Alloys Containing Aluminium. Marc Chirade and Joseph Canac, Paris, France. Patented July 2, 1912.
- 1,030,999. **Refractory Article** and Method of Making It. Samuel F. Hall, Niagara Falls, N. Y., assignor to Norton Company, Worcester, Mass., a corporation of Massachusetts. Patented July 2, 1912.
- 1,031,0003. **Waterproofing** Compound. Aron C. Horn, New York, N. Y. Patented July 2, 1912.
- 1,031,017. Economic Process of Producing **Gas**. Max Mauran, Niagara Falls, and James H. McMahon, La Salle, N. Y. Patented July 2, 1912.
- 1,031,074. Production of **Oxalic Acid**. Frank Austin Lidbury, Niagara Falls, N. Y. July 2, 1912.
- 1,031,153. Method of **Sintering Fine Ores** and Similar Materials. James G. West, Jr., Wilksburg, Pa. Patented July 2, 1912.
- 1,031,413. Utilizing Acid Sludge from **Refining Petroleum**. John C. Black and Marvin L. Chappell, Richmond, Cal., assignors to Standard Oil Company, Richmond, Cal., a Corporation of Cal. Patented July 2, 1912.
- 1,031,477. Process of Binding and Utilizing **Air-Nitrogen**. Alf Sinding-Larsen, Christiania, Norway, assignor to Messrs. Storm, Bull & Co., Christiania, Norway. Patented July 2, 1912.
- This is a process of binding and utilizing atmospheric nitrogen, by treating oxid materials, together with a reducing agent at a raised temperature with substances consisting of or containing elements capable of forming volatile compounds with the base of said oxid material and treating the obtained volatile compounds with nitrogen at a raised temperature.
- 1,031,490. Reductions of **Ores**. Elihu Thomson, Swampscott, Mass., assignor to General Electric Company, a Corporation of New York. Patented July 2, 1912.
- 1,031,581. Compound of **Aluminum Carbon and Nitrogen**. Samuel Peacock, Chicago, Ill., assignor to E. I. du Pont de Nemours Powder Company, a Corporation of New Jersey. Patented July 2, 1912.
- 1,031,582. Process of Producing **Ammonia**. Samuel Peacock, assignor to E. I. du Pont de Nemours Powder Company, a Corporation of New Jersey. Patented July 2, 1912.
- 1,031,814. Process of Producing Plastic Substances from **Milk**. Ottokar Henry Nowak, Chicago, Ill., assignor to Francois Lebreil and Raoul Desgeorge, Lyon, France. Patented July 9, 1912.
- 1,031,837. Process of Manufacturing **Caout-chouc-like Products**. Arnaldo Caroselli, Florsheim-on-the-Main, Germany, assignor to the firm of Chemische Fabrik Florsheim Dr. H. Noerdlinger, Florsheim-on-the-Main, Germany. Patented July 9, 1912.
- This is a process of manufacturing caout-chouc-like products which consists in treating a mixture of oxidized oils and loading materials in the presence of a condensation agent with an aldehyde.
- 1,031,864. Method of Concentrating **Nitric Acid**. Harry Pauling, Gelsenkirchen, Germany, assignor to Salpetersaure-Industrie-Gesellschaft, G. M. B. H. Gelsenkirchen, Germany. Patented July 9, 1912.
- 1,032,151. **Bleaching Process**. Eugene L. Maypai, New York, N. Y. Patented July 9, 1912.
- 1,032,229. Process for **Bleaching** Old Papers, Paper-Stock, Straw, etc. John H. Melchers, Decatur, Ill. Patented July 9, 1912.
- 1,032,242. **Explosive**. Williams Rickmers, London, England. Patented July 9, 1912.
- 1,032,246. **Method of Treating Carbon**. William Acheson Smith, Niagara Falls, New York. Patented July 9, 1912.
- 1,032,392. Process of Producing **Fermentable Sugar** from Lignocellulose. Malcolm F. Ewen and George H. Thomson, Chicago, Ill., assignors to Standard Alcohol Company, New York, N. Y., a Corporation of Maine. Patented July 16, 1912.
- 1,032,400. Process of Treating **Ores**. Wilhelm Gunther, Cassel, Germany. Patented July 16, 1912.
- 1,032,642. Tasteless **Quinin Compound** and Process of Making Same. Lorenz Ach, Mannheim-Waldhof, Germany, assignor to C. D. Boehringer & Soehne, Mannheim-Waldhof, Germany. Patented July 16, 1912.
- 1,032,653. Method of Manufacturing **Steel**. Herman A. Brassert, Braddock, Pa. Patented July 16, 1912.
- 1,032,763. Process of Making **Fertilizer**. Spencer B. Newberry and Harvey N. Barrett, Baybridge, Ohio. Patented July 16, 1912.
- This is a process of rendering insoluble phosphates citrate-soluble by calcining them with carbon until the carbon is consumed, and calcining them further in an oxidizing atmosphere at nearly white heat.
- 1,033,051. Method of Reducing **Iron Ore**. Gustaf Grondal, Djursholm, Sweden. Patented July 16, 1912.
- 1,033,064. Process of Producing **Fermentable Sugars**. Francis E. Gallagher, Newton, and Harry S. Mork, Boston, Mass., assignors to Arthur D. Little, Incorporated, Boston, Mass. Patented July 16, 1912.
- 1,033,285. **Explosive Charge**. Ernst Sokolowski, Hamburg, Germany, assignor to E. I. du Pont de Nemours Powder Company, Wilmington, Del., a Corporation of New Jersey. Patented July 23, 1912.
- 1,033,359. Process for **Extraction of Gold** from Clay. Jacobus Jan William Hendrik van der Toorn, The Hague, Netherlands. Patented July 23, 1912.
- 1,033,405. Production of **Lead Compounds**. Louis S. Hughes, Chicago, Ill., assignor to Picher Lead Company, Joplin, Mo., a Corporation of Missouri. Patented July 23, 1912.

- 1,033,537. **Safety Explosive.** Norbert Ceipek, Vienna, Austria-Hungary. Patented July 23, 1912.
- 1,033,565. **Aluminum Solder.** Charles R. Erkens, New York, N. Y., assignor to Simplex Aluminum Solder Company, Inc., New York, N. Y., a Corporation of New York. Patented July 23, 1912.
- 1,033,904. **Arseno Compounds and Process of Making Same.** Robert Kahn, Frankfort-on-the-Main, Germany, assignor to Farbwerke vorm. Meister Lucius & Bruning, Höchst-on-the-Main, Germany, a Corporation of Germany. Patented July 30, 1912.
- 1,033,927. **Blasting Powder.** Richard Ponnay, Los Angeles, Cal., assignor of one-fourth to John F. Hubbard, Los Angeles, Cal. Patented July 30, 1912.
- 1,033,984. **Method of Manufacture of Hydraulic Cement.** Frederick W. Brown, Florence, Colorado, assignor of one-half to Louis M. Schmidt, Hartford, Conn. Patented July 30, 1912.
- 1,034,018. **Manufacture of Tungsten Filaments for Incandescent Electric Lamps.** Anton Lederer, Vienna, Austria-Hungary, assignor to Westinghouse Lamp Company, a Corporation of Pennsylvania. Patented July 30, 1912.
- 1,034,036. **Process of Producing Food Fats.** Peter Adam Schmidt, Hamburg, Germany. Patented July 30, 1912.
- 1,034,090. **Art of Converting Phosphorites.** Henry V. Dunham, Bainbridge, N. Y., assignor to Nacirema Chemical Company, a Corporation of Vermont. Patented July 30, 1912.
- 1,034,281. **Process of Obtaining Potash from Feldspar.** James Miller Neil, Toronto, Ontario, Canada, assignor to Alexander M. Hay, Toronto, Canada. Patented July 30, 1912.
- The process consists in melting the mineral together with a sulfate metal; and subjecting the molten mass in the presence of steam or air to the action of a gaseous sulfur compound containing oxygen.
- 1,034,283. **Tanning Compound.** Birt W. Newman, Rocky Ford, Colo., assignor of one-third to Allen L. Turnipseed, Yampa, Colorado. Patented July 30, 1912.

WANTS.

POSITION WANTED—Junior chemist, desires position as assistant or in charge. Two years' experience in iron, steel and oils. Excellent references. Metallurgist. care of Chemical Engineer, 608 So. Dearborn St., Chicago, Ill.

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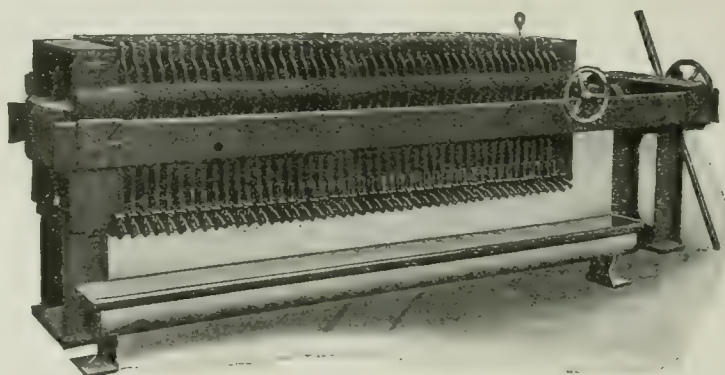
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THE WORK OF A MUNICIPAL GAS TESTING STATION.

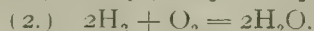
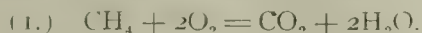
By EDWARD K. HAMMOND.

(Concluded from September issue.)

To explain the method of making the calculation of the results of the analysis, an average set of figures for the analysis of a carburetted water gas will be assumed.

Volume of gas taken for analysis.....	101.65 cc.
Volume after leveling manometer.....	100.05 cc.
Volume after absorbing carbon dioxide.....	97.15 cc.
(2.90% carbon dioxide)	
Volume after absorbing illuminants.....	84.00 cc.
(13.15% illuminants)	
Volume after absorbing oxygen.....	83.80 cc.
(0.20% oxygen)	
Volume after absorbing carbon monoxide.....	55.05 cc.
(28.75% carbon monoxide)	
Volume of air taken for explosion.....	85.00 cc.
Volume of air + gas for explosion.....	99.00 cc.
Volume of gas for explosion.....	14.00 cc.
Volume after explosion.....	76.50 cc.
Volume after absorbing carbon dioxide.....	71.10 cc.
Percentage of methane by calculation.....	25.20%
Percentage of hydrogen by calculation.....	25.95%
Percentage of nitrogen by difference.....	3.80%

The calculation of carbon dioxide, illuminants, oxygen, and carbon monoxide is merely a matter of subtraction. The calculation of methane and hydrogen is rather more involved, the method being based upon the chemical reactions governing the manner in which these gases react with oxygen when the explosion takes place. These reactions are shown below:



For the calculation of methane, it will be seen from equation (1) that one volume of carbon dioxide results from the explosion of each volume of methane, because under the same conditions of temperature and pressure equal volumes of gases have the same number of molecules. From the explosion of 14.00 cc. of gas it was found from the result of the analysis that 6.4 cc. of carbon dioxide was produced. After completing the absorption of the carbon monoxide, it will be remembered that there was 55.05 cc. of gas left. Therefore, this residual gas, which contained all of the methane which was originally present in the sample taken for

analysis has $6.4 \div \frac{55.05}{14.00} = 25.20$ cc., which represents 25.20 per cent of methane in the gas.

Referring to equation (2) it will be seen that two

volumes of hydrogen unite with one volume of oxygen to produce zero volumes of water vapor. It is also seen from equation (1) that one volume of methane unites with two volumes of oxygen to form one volume of carbon dioxide and zero volumes of water vapor. In order to arrive at the portion of the total contraction in volume which took place during the explosion, that was caused by the hydrogen in the gas, it is necessary to refer to the original figures for the analysis. Here it will be seen that the volume of air plus gas delivered to the explosion pipette was 99.00 cc., while 76.50 cc. of residual gas was returned to the burette. This gives $99.00 - 76.50 = 22.50$ cc. as the volume of the contraction which took place as the result of the explosion. This contraction is due to the combination of the methane and hydrogen in the gas with the oxygen supplied for the purpose of exploding them. It has been noted that the explosion of the methane results in the production of one volume of carbon dioxide and two parts of water vapor having zero volume. Thus the total contraction resulting from the explosion of the methane is seen to be twice the volume of the carbon dioxide produced or $2 \times 6.4 = 12.8$ cc. Subtracting this volume from that of the total contraction gives $22.50 - 12.80 = 9.70$ cc. as the volume of the contraction due to the explosion of the hydrogen in the gas. It has been shown that this contraction represents three-halves of the volume of hydrogen present in the gas. Consequently the total volume of hydrogen present in the sample of gas that

was taken for analysis is $\frac{2}{3} \times \frac{55.05}{14.00} \times 9.70 = 25.95$

cc., or 25.95 per cent of hydrogen in the gas. In this calculation it will be seen that the method of converting the contraction due to the hydrogen in the 14.00 cc. gas sample taken for explosion to what it would have been for the entire 55.05 cc. of residual gas is the same as formerly explained for the methane calculation.

Fig. 7 shows a modified form of the "Referee's" apparatus for the determination of the amount of ammonia and sulphur carried by a gas supply. The name comes from the fact that it was designed by the referee chemist who was engaged to fix upon standards for the gas supplied to the city of London, England. The modifications in the apparatus shown in Fig. 7

from the original design lie in the trumpet tube and cooling tower filled with glass marbles. In the apparatus illustrated, the trumpet tube is larger than the ones originally used and is turned down at the point where it enters the cooling tower. This arrangement



Fig. 7—The Referee's Apparatus for Total Sulphur and Ammonia.

changes the direction of flow of the gases resulting from the combustion of the gas and ensures a complete absorption of the sulphur. The cooling tower itself is also larger, thus giving more surface for the sulphur to collect upon.

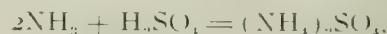
In using this apparatus, the two small bottles shown in the tubing leading to the meter are filled with N/10 sulphuric acid. The gas bubbles through this acid on its way to the meter and any ammonia which it carries is absorbed. The quantity is then easily determined by titrating the excess acid with standard potash. The gas next passes through the meter and the dry pressure regulators and is burned through the tip located under the trumpet tube. Any sulphur present in the gas is oxidized and absorbed along with the water which condenses in the cooling tower. This absorption is facilitated by placing some ammonium carbonate around the burner during the time that the apparatus is working. This carbonate evaporates slowly and produces an alkaline atmosphere which fixes the acid sulphur fumes. Approximately ten feet of gas is burned, the rate being so regulated that the combustion takes about twenty hours, and after the completion of the run, the apparatus is thoroughly flushed out with distilled water. These washings are collected in the flask at the bottom of the cooling tower and are treated in the usual manner for the determination of sulphur as barium sulphate. The results of both the determina-

tion of ammonia and sulphur are expressed in grains per one hundred cubic feet of gas.

Assuming the volume of gas burned during the test to have been 10.215 cu. ft., the weight of the barium sulphate produced to have been 0.2596 grams, and knowing that there are 15.43 grains in a gram, and that the sulphur factor for barium sulphate is 0.1376, the number of grains of sulphur in 100 cu. ft. of the gas at the time the test was made is found to be

$$\frac{0.2596 \times 0.1376 \times 15.43 \times 100}{10.215 \times 0.950} = 5.04.$$

In the absorption of ammonia by sulphuric acid, the reaction takes place according to the following equation:



where thirty-four parts of ammonia are taken up by forty-nine parts of sulphuric acid.

Each cubic centimeter of the — sulphuric acid used contains .049 grams of H_2SO_4 and has been exactly balanced against the — potassium hydroxide solution that is used to titrate the excess acid.

For use in making a sample calculation it is assumed that ten cubic centimeters of the — acid was placed in the absorption bottles of the Referee's apparatus and after the test 9.5 cc. of KOH solution was

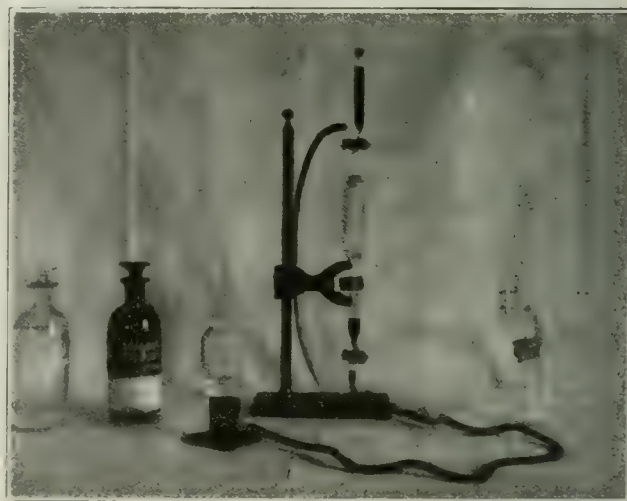


Fig. 8—Apparatus for Quantitative and Qualitative Tests for Hydrogen Sulphide.

used to neutralize the excess acid. Consequently there was 0.5 cc. of acid neutralized by the ammonia present in the gas, the amount of this ammonia being

$$0.5 \times \frac{49}{34} \times \frac{1}{10} = 0.0353 \text{ grams of ammonia. There}$$

were 10.215 cu. ft. of gas burned and the correction factor for the temperature and pressure conditions at

the time of the test was 0.956. This gives the number of grams of ammonia per hundred cu. ft. of gas as

$$\frac{0.0353 \times 100 \times 15.43}{10.215 \times 0.956} = 5.55.$$

A gas which has been properly purified should not have more than ten grains of ammonia and twenty grains of sulphur per 100 cu. ft.

Fig. 8 shows Tutwiler's apparatus for the quantita-

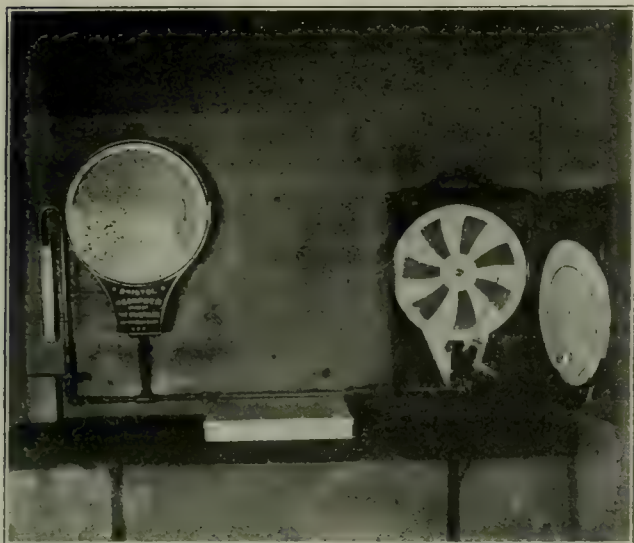


Fig. 9—An Installation of Recording Bristol Pressure Gauges.

tive determination of hydrogen sulphide by titration with standard iodine solution, each cc. of which has been made to equal 100 grains of hydrogen sulphide per 100 cu. ft. of gas. In making this determination the leveling bottle is filled with starch solution. The cocks at the top and bottom of the burette are then opened and the leveling bottle is then raised until the starch solution has filled the burette and flows out of the gas inlet. The cocks are then closed and the leveling bottle lowered. The gas inlet tube is then connected with the gas supply to be tested, as shown in the illustration, and the cocks at the top and bottom of the burette are opened until the gas has just passed the 100 cc. graduation at the bottom of the burette. The cocks are then closed at the bottom and top of the burette, and the gas supply is disconnected. The lower cock is next opened and the leveling bottle raised until the level of the starch solution is just at the 100 cc. mark on the burette. The cock at the top of the burette is then opened and immediately closed; this allows sufficient gas to escape so that there is just 100 cc. in the burette under atmospheric pressure. The leveling bottle is now lowered until the starch solution has dropped to the 110 cc. graduation on the burette; the lower cock is now closed. This places the gas in the burette under a negative pressure.

The graduate at the top of the apparatus is now filled with the standard iodine solution. Owing to the fact that the gas in the burette is under a slight negative pressure, it is possible to run the iodine solution

in through the connection in the stop cock between the graduate and the burette. The titration is conducted with constant shaking until the end point is reached, as shown by a permanent purple coloration of the starch solution in the bottom of the burette. The exact volume of iodine solution is then noted and, from its volume, the number of grains of hydrogen sulphide per 100 cu. ft. of gas is easily calculated.

Most city ordinances require the gas to be practically freed from hydrogen sulphide. Consequently, a rapid method of making qualitative tests for this constituent is of more value in a municipal laboratory than the results obtained with the Tutwiler apparatus just described. At the right hand side of Fig. 8, a convenient form of apparatus for this purpose is shown. The gas is brought to a pressure of $1\frac{1}{2}$ ins. of water, as indicated by the small manometer, and is allowed to impinge upon a moist sheet of lead acetate paper held at a distance of $\frac{1}{2}$ in. from the bent tube. If the gas has not been properly purified, a brown stain of lead sulphide will be produced, which shows that there is an objectionable amount of hydrogen sulphide present.

The lead acetate paper for this test is made by dipping sheets of filter paper in a solution of lead acetate. After the paper has dried out it is cut up into strips ready for use. The paper is moistened with ammonia water before using.

PRESSURE TESTS.

The most convenient way of determining the pressure conditions throughout the city is to have a num-

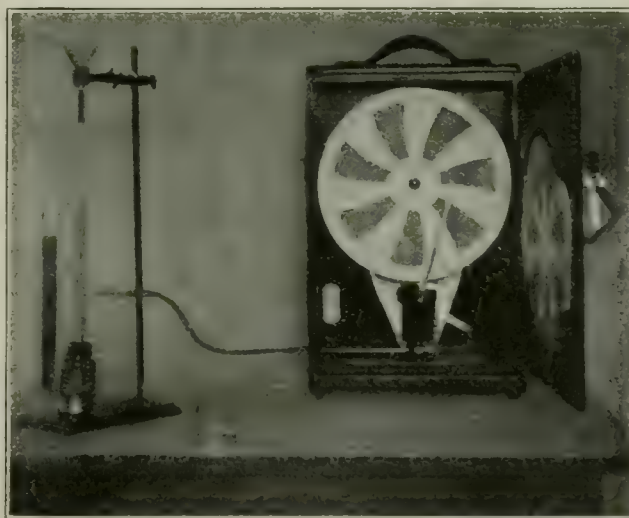


Fig. 10—Apparatus Used for Calibrating Pressure Gauges. Arrangement of Apparatus.

ber of recording gauges set in different locations. These gauges can be shifted about at short intervals so that a knowledge is gained of the pressure at which the gas is being supplied at a number of representative points.

Fig. 9 shows an installation of a 24-hour and a 7-day gauge with a manometer located on the same piping so

that the indications of the gauges can be verified at any time. As previously mentioned, good laboratory practice requires all apparatus to be accurately calibrated to verify the work of the manufacturer. Fig. 10 shows the method used to test the recording pressure gauges of the type shown in the illustration. The small glass bottle standing at the base of the ring stand is fitted with a three-hole rubber stopper which carries the connection for the rubber tube leading to the gauge, the manometer, and the tube connecting with the small funnel suspended over the bottle. By pouring mercury into the funnel, the air in the bottle is put under pressure, and this pressure is communicated to the gauge through the rubber tubing. The indication of the gauge can thus be checked against the manometer which is subject to the same pressure which throws over the needle on the dial of the recording instrument.

By adding a little mercury at a time, the pressure can be gradually increased to cover the entire range of the recording pressure gauge. At each step in the process, readings are taken on both the gauge and the manometer, thus verifying the accuracy of the indications of the former. Absolute assurance is thus gained that the gauge is giving the proper readings and the possibility of an error in setting on the part of the manufacturer is avoided.

Referring to the extraordinary growth of the demand for glazed kid and other goatskin leathers in recent years and the somewhat limited supply of suitable raw material, the Leather Trades Review discusses the question of rearing goats for the leather industry and establishing various subsidiary industries for the use of the by-products. The periodical suggests that the hardy nature of goats permits them to thrive on scanty vegetation, that they are at their best in hilly or mountainous districts which are almost entirely unsuitable for cultivation, and that no other domestic animals of any importance to the leather industry can be reared so economically. Yet the goat supply of the United Kingdom is so insignificant that no reference is made to them in the statistics of the live stock industry published by the Board of Agriculture. The Review further expresses the opinion that if the goat industry were seriously taken up in the United Kingdom there would be both a stouter and a stronger type of pelt for the leather industry, a type of goatskin that is so difficult to find at present, and then argues that the breeding and rearing of goats could easily be a very profitable industry, that it offers enormous possibilities for the extension of the British light-leather industry and that the characteristics of the raw skins would be of a type to meet the urgent requirements of shoemakers and of the public demand for a stouter leather with stronger fibrous texture.

THE MODERN SEWAGE AND WATER PROBLEM.*

By DR. ARTHUR LEDERER.†

It is hardly possible to discuss the sewage and water problems separately. The two are so intimately connected that no sharp line of demarcation can justly be drawn. It is true that many communities with a water problem have no sewage problem to solve, but this is because they have shifted their sewage problem upon the shoulders of neighboring communities, which are willing to stand for it as long as no actual nuisance from odors ensues, or as long as no economic loss results, such as through pollution of oyster beds. The economic loss to the community at large from disease or death is discounted, or overlooked, until the public conscience is aroused by a severe epidemic. Only a few large communities in this country, such as Chicago, are in so fortunate a position as to be able to discharge their sewage into a stream without being responsible for any economic losses, as mentioned above, or without forcing a water problem on other cities bordering the stream. Again, but few cities take, as yet, their water supply from streams in which self purification has taken place to such a degree as to make the water reasonably safe.

In order to appreciate the present state of the water and sewage problems, and in order to prognosticate with a fair degree of authority what the ultimate solution will be, one has to look back and study the history of the problem. The history of water supply coincides in a general way with the history of sanitation. Water-borne epidemics must have existed long before any mention was made of them, and it is only in comparatively modern times that water has become firmly recognized as the most important vehicle for disease. We know that the Romans took great care in providing a good sparkling water supply, building extensive and costly aqueducts, some of which were built 300 B. C., and are in use for the same purpose today. It is likely that aside from the aesthetic reason for obtaining a clear, sparkling water supply, the instinct of the danger lurking in a turbid water might have played a part. Good water supplies could be found in the Orient in very early times. Water conduits existed in Ninevah and Tyros (Syria) as early as 700 B. C. Jerusalem, Damascus, and Athens had water conduits in early days, and Pergamon even possessed a high-pressure water system. Originally wells and cisterns constituted the sole water supply. Some of the old Pharaonic Egyptian wells are in a good state of preservation up to this day.

During the middle ages, even up to the nineteenth century, the improvements in water supplies were of a technical nature, and not very revolutionary. Water pumps, which came more generally into use in the 16th and 17th centuries, were improved, and so were

*Paper read at the Annual Meeting of the Illinois State Homeopathic Medical Society, May 14-16, 1912.

†Chemist and Bacteriologist, The Sanitary District of Chicago.

other technical features, but it remained for the young science of biology, some 50 or 60 years back, to open our eyes to the great dangers from a polluted water supply, and to lead the way to its elimination. Johann Peter Frank, in his treatise, "Von der Pflege des Trinkwassers und der Brunnen," published in 1792, gave first what might be called the modern conception of a sanitary water supply. As may be easily surmised, a great many of his conceptions did not hold good in the light of later experiences and investigations. It is interesting to note that he condemned hard waters as being detrimental to health. He considered spring waters the best supply, and then the waters of large rivers. It is peculiar that the ground water which is now looked upon as one of the safest sources of supply was regarded by him with skepticism. He recommended an annual thorough chemical examination of the water, and was heartily in favor of boiling a polluted water previous to permitting it to percolate through sand. Frank warned against the pollution of wells, and called attention to the necessity of judging the water supply of the community by the general health of its citizens. This was over 100 years ago. Today our conception of the etiologic factors involved has been put on a firm basis, and the science of hydraulic engineering is endeavoring to adjust itself to the valuable discoveries in the field of biology, which add continuously to our knowledge.

We look down with contempt upon the poor Hindu who poisons himself with the sacred waters of the Ganges, and who, in his orthodox convictions, does not realize that the bathing of cholera-infested people in a river which is used for a water supply conflicts with the fundamental principles of sanitation. Yet, to a lesser degree, conditions such as that, exist in our own country, and we shut our eyes to the dangers confronting us from infection by water-borne disease. Asiatic cholera can, of course, be considered as stamped out in civilized countries, save a few sporadic cases, which are promptly taken care of. Its place has been taken by typhoid fever, the prevalence of which can safely be looked upon as an index of the civilization and progressive spirit of a country. Europe, with its paternal system of government, has taken the lead in the sanitation of water and sewage. The first studies of the effect of an improved water supply originated largely in England and Germany. A recent publication by Dr. Dunbar, of Hamburg, which appeared in the *Gesundheits Ingenieur* ("Zum gegenwärtigen Stande der Oberflächenwasserversorgung" 35: 185-96; 220-24), illustrates well the relation of an improved water supply to public health. Many of the figures quoted in the following lines appear in his article. In 1877 the statistics of 149 German cities showed an average typhoid fever death rate of 46 per 100,000 population. In 1900, a survey of 349 cities showed only 5 deaths per 100,000. This reduction was mainly due to the improvement in water supplies. In the period 1831 to 1873, 373,000 people died in Prussia of Asiatic cholera (in 1886 alone, 111,000).

In 1892, when cholera again appeared, Prussia had but 1,634 deaths. Hamburg suffered the penalty for its neglect of filtering the water supply; 8,616 people died of cholera in Hamburg during that year. Perhaps never has the value of water purification been more forcibly illustrated than during that epidemic. Altona, adjoining Hamburg, had a filtered water supply, and as a consequence escaped the epidemic. Today the German sanitarians have the situation so well in hand that a repetition of the 1892 experience is hardly possible, and the few cases of cholera which can be found every year on German territory do not increase. In 1910 Germany had but ten cases of cholera. Beyond a doubt, the improved water supply is largely responsible for this satisfactory state of affairs, although improvements in the other branches of hygiene and sanitation are also important. The installation of new water supplies in Berlin, Halle, Danzig, Breslau, Frankfort am Main, Dresden, Elberfeld, Munich and Hamburg has, in all instances, been followed by a distinct decrease in the typhoid fever death rate. Rates which used to be anywhere from 60 to 130 per 100,000 dropped remarkably after the installation of the new water supply. Today they correspond to figures below 10, and in some instances go as low as 1 per 100,000.

The oldest method of water purification on a large scale originates from England. It consists of a fine sand filter, built over a layer of gravel and stone, and was devised by James Simpson. The filter proved so satisfactory that it was installed in the Chelsea Water Works (London). In 1853 Berlin built a Simpson filter, and other cities followed shortly. The original intention was to obtain a water supply largely improved in its physical characteristics, but not so much thought was given at that time to the bacterial improvement. Gradually it became recognized that bacterial removal was of prime importance, and Simpson's filter was considered bacteria proof until 1890. In that year Karl Frankel and C. Piefke published the results of their experiments, in which they showed that Simpson's filter, even if intelligently operated, did not retain completely such organisms as the typhoid fever bacillus and the cholera spirillum. A heated controversy followed, but other investigators were quick to substantiate Frankel's findings. It was found that the bacteria were greatly reduced, but still the species were present in the effluent. At that time the quantitative feature of the mode of infection was not considered. The very presence of the bacillus after such a severe artificial test in the effluent of the filter was then deemed sufficient to condemn this process of purification. Today we recognize that the quantitative feature must be considered in connection with the possibility of infection, although definite knowledge and substantiative experimental work is still largely lacking. This question was splendidly discussed in a paper read by Charles V. Chapin at the annual meeting of the American Public Health Association, at Richmond, Va., in 1909. The title of

the paper reads, "The Need of Quantitative Methods in Epidemiological Work."

The technique of the installation of sand filters has been greatly improved since 1890, but Robert Koch persistently advocated a ground water supply in preference to sand filters, with the result that no large filter works have been built in Germany since 1900. Whenever possible German cities resort to ground water. Still, a comparison of the typhoid fever death rates between cities using a filtered water and those using ground water does not show a material difference. Six large German cities with sand filters had, in 1910, a typhoid fever rate of 4.4 per 100,000. Twenty-five large German cities with ground water supply, in the same year, had a typhoid fever death rate of 3.6 per 100,000. This country is not as fortunate with its typhoid fever death rate, although here, as abroad, the remedy is the same. We put forth a lot of excuses, such as, "We have grown too quickly, give us time," or we blame lack of available funds. But what we really need is a great central powerful body, such as exists in German states, to steer us right on the a, b, c of sanitation. The lack of a central authority in sanitary matters has proven very costly to us, and this situation will continue until we recognize the fact that health should be put above the dollar, and until we are in a position to force sanitary improvements upon the ignorant to protect them against themselves.

As could be reasonably expected, sanitation in this country took a foothold a good deal later than it did abroad. In 1870 no important city had a filtered water supply. In 1910, 10.8 million people were supplied with filtered water. In contradistinction to German conditions, our supply is mainly a surface water supply. Some 50 years back the typhoid fever mortality in North American cities varied between 50 and 100 per 100,000. For the period 1901 to 1905 the average mortality was 46 per 100,000, against 7.6 for Germany for the same period. In 1910, 28.2 per cent of the city population in the U. S. was supplied with filtered water, and the average typhoid fever death rate dropped considerably, but not anywhere near German figures, possibly with the exception of Cincinnati.

That good results can be accomplished by filtration of water supplies in this country can well be illustrated by the following figures. Before a change in the water supply, the average typhoid fever death rate of Providence, R. I., St. Louis, Mo., Youngstown, O., Ithaca, N. Y., Paducah, Ky., Watertown, N. Y., Paterson, N. J., and Binghamton N. Y., was 64.7 per 100,000. The year after the introduction of the improved water supply the average figure dropped to 29.9, which constitutes an improvement of 53.8 per cent. These figures speak for themselves. To what extent they can still further be reduced by additional improvements in the water supply, or to what extent the improvement in the water supply would serve to reduce the general death rate, are special

problems worthy of the most careful study. That these figures are capable of improvement no one will doubt.

The so-called rapid sand filters, or mechanical filters, in contradistinction to slow sand filters have met with great favor in this country. The process consists in preliminary sedimentation, and the addition of coagulants to hasten the settling process before permitting the water to reach the filters. The bacterial results have been very satisfactory, and the system has attracted a good deal of attention recently in Germany, where it is not always practicable to obtain a satisfactory ground water. Of importance also are the results of A. C. Houston, of London, showing the great reduction of pathogenic bacteria in a reservoir with long storage. Houston found that typhoid fever bacilli are eliminated after four to six weeks' storage, making such a supply safe even without following filtration. This would tend to show that a water supply from an impounded reservoir or from a small inland lake with a well protected watershed constitutes a reasonably safe surface water. Aside from such rare exceptions, however, there is only one safe principle to apply, and that is to assume that all surface waters at all times, or at some time, are unsafe for drinking purposes, and should not be allowed to reach the consumer without previous treatment.

The sterilization of a water with ozone and by the aid of ultra violet rays has not been a practical success as yet, for economic reasons and on account of technical difficulties.

The purification of sewage is undertaken to protect a water supply, to avoid nuisance, to prevent contamination of shell fish, or to preserve a fish industry. The water as supplied to the consumer must be beyond suspicion, but the purification of sewage presents an individual problem, for which no definite rule can be given to be applied or followed. The ideal state would be to purify the sewage to its highest degree, and to sterilize the final effluent to make it perfectly safe for drinking purposes, but such treatment is costly, and one rarely required. In most cases partial purification will suffice.

In many cases a great deal of good can be gained by the co-operation of neighboring communities, because the sewage problem is rarely the problem of a single community. Unfortunately here too, the lack of authority invested in a central sanitary body in this country has been a detriment. So-called sanitary districts, organized for the protection of fisheries and for the economical disposal of sewage, exist abroad, as well as in this country. In Boston, the Metropolitan Sewerage Commission controls the main sewerage of the city of Boston proper, and of Brookline, Cambridge, and other independent municipalities near Boston. The Commissioners are appointed by the governor of the state. Each city manages its own local sewerage. The expense of the work of the commission is estimated every five years, and assessed upon the individual cities and towns by a special commit-

tee appointed by the Governor for that purpose. In 1895-6 the Passaic Valley Sewerage District was created by state law. The district was intended to control the sewerage of this district, and to prevent the pollution of the Passaic River. Owing to much opposition to entire state control, and other reasons, the district has not been put on a good working basis. Some New Jersey cities, however, have co-operated in building common sewers.

The First German sanitary district, with a more flexible charter than that of any other district, was formed to deal with the sewage of the drainage area of the Emscher river, with headquarters at Essen. The district covers an area of 308 square miles, and has a population of about two million. This "Emschergenossenschaft" was organized by a law passed in 1906. It is empowered to compel cities in the district to provide and maintain suitable sewerage systems, to compel the discharge of trade wastes into sewers, and to establish cesspools. It has the right to build sewers and purification works. The cost is apportioned among the cities according to "responsibility for existing objectionable conditions, and benefits to be derived." No other similar organization exists in Germany or anywhere else, but it has proven so successful that it is likely to be duplicated. The whole of England, as of Wales, outside the city of London, is divided into administration districts, called counties, or boroughs. For sanitary administration the boroughs are deemed to be urban districts, and, with the other urban districts, constitute the urban sanitary district. Rural sanitary districts exist likewise. The sewerage is under the control of the local sanitary authorities of these various districts. London had a Metropolitan Board for the construction of the main sewerage and drainage system. In 1899 this board was succeeded by the London County Council, which is the controlling sanitary authority. In some instances several sanitary districts have co-operated in forming a district board, as for instance the Birmingham, Tame and Rea districts, including the city of Birmingham and the West Riding of Yorkshire district.

The largest sanitary district in the world is the Sanitary District of Chicago, established primarily for the purpose of sewage disposal by dilution. The formation of such districts is of incalculable value, particularly to smaller communities which are willing to pay their share to relieve a live nuisance, and which are not financially strong enough to take the initiative.

Similar districts exist here also for the supplying of a good wholesome water to an aggregation of communities.

The science of sewage purification is comparatively young, and its progress has been greatly influenced by the over-congestion of certain communities, and by the rapid development of industry here as well as abroad. The "septic tank" scheme of sewage disposal is on the wane. Some 15 years ago it was hailed as the panacea for all the difficulties in sewage purifi-

cation, but today we know that the claims for the "septic tank" are greatly exaggerated, and that the digestion of sludge is a very variable factor, and by no means as complete as some observers would make us believe. Aside from the possibility of a nuisance, and the unloading of sludge during summer, we also have recognized that a sewage should be fresh for subsequent treatment on sprinkling filters or oxidizing beds of any kind, and this had led to the introduction of the so-called "Emscher tank." These are double deck tanks of German origin, which furnish a fresh effluent, and in which sludge digestion takes place in a separate subjacent sludge digestion chamber. Some 40 plants of this kind are being built in Germany at the present time, and several in this country, the largest in Atlanta, Ga. Two Emscher tanks are also operated in the sewage testing station of the Sanitary Districts of Chicago.

Sewage treatment in septic tanks, or settling tanks, accomplishes only partial purification, and should be followed, for more complete results, by oxidation processes and secondary settling basins. But such an effluent will not furnish water of a good sanitary quality, although it is very often sparkling and clear. The bacteria must be destroyed by a disinfection process—for instance, by chlorinated lime—before allowing the effluent to reach a water supply. By itself a disinfected effluent would be safe for drinking purposes, but it would justly be rejected for psychological reasons, if for no other. The oxidation of a partly purified sewage has been practiced for the last 30 years, but the disinfection of sprinkling filter effluents, or of a contaminated water supply with chlorinated lime is of very recent origin.

The disinfection of an impure water supply with chlorinated lime is working wonders in the reduction of typhoid fever death rates, and quite a number of cities bordering on the Great Lakes have resorted to it with great success. The treatment is cheap and effective, but it should not supplant the more reliable sand filtration, or mechanical filtration for any length of time. The reason for this is simple. Even a short interruption in the disinfection process may permit the infection of the consumer, while a sand filter, even if not properly operated at all times, will always be a great improvement over the raw water. So far as I am aware, sprinkling filter effluents have never been subjected to disinfection on a practical scale, here or abroad, but the disinfection of sewage for the protection of the shell fish industry is practiced in some places on the coast, such as in Red Bank, N. J.

Electrical schemes of sewage disposal have never been a success, in spite of the high development of the science of electricity. The few places which installed such schemes and claimed success have not withstood the searching investigation of the economist and engineer.

The disposal of sewage sludge is still a problem which awaits satisfactory solution. At present we dispose of it by drying it on sand beds and use it to fill

in low lands. In a few places abroad it is sold for fertilizer, or given away to farmers, but the experience has been that in the second year the farmer, as a rule, did not care to haul it away free of charge.

It is impossible for me, in the short time at my disposal, to more than merely outline to you the main features of the great modern water and sewage problems. I wish to emphasize strongly that too little has been accomplished in this country as yet. We could easily cut the typhoid fever death rate in half by paying more attention to the purification of water supplies and the prevention of sewage pollution. We have a well-developed technique at our disposal. Our engineers and biologists are no longer in the dark, but our moral perceptions and responsibilities need a rude awakening. Let us hope that in the near future a National Board of Health, or some body with a well defined authority in sanitary matters, exceeding the authority in interstate affairs, will help us to put the United States among the nations which can proudly point to a low typhoid fever death rate as a just measure of their civilization.

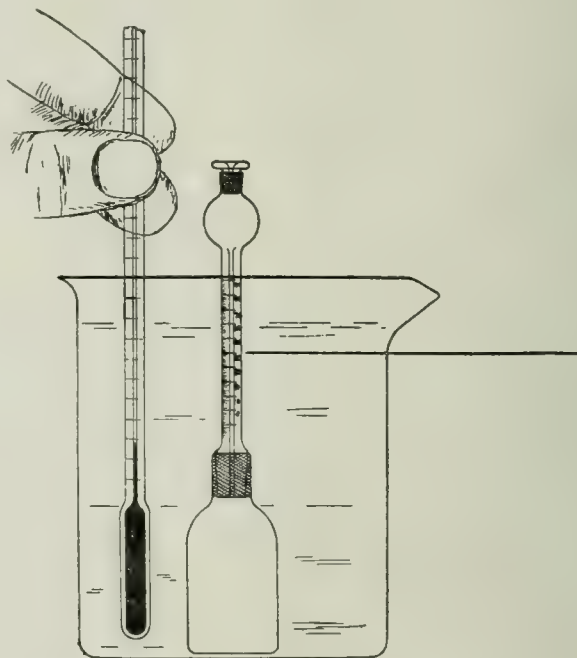
From 1814, the date of the earliest record of coal production in this country, to 1911, inclusive, according to a chart just issued by the United States Geological Survey, Pennsylvania has furnished 2,270,798,737 short tons of anthracite coal and 2,396,491,260 short tons of bituminous coal, a total of 4,667,289,997 short tons. The greatest output of anthracite coal from this state was in 1911, when 90,464,067 short tons were mined; the record production of bituminous coal was in 1910, when the yield was 150,521,526 short tons. Illinois ranks second in the production of coal during the period from 1814 to 1911, with 844,012,353 short tons of bituminous coal; West Virginia third, with 649,448,201 short tons; and Ohio fourth, with 611,949,292 short tons. None of the other states has produced as much as 500,000,000 short tons during the period. These four states have therefore produced during the 98-year period 6,772,699,843 short tons of coal, or more than three-fourths of the total output of the United States.

There was a decrease of nearly 28 per cent in the production of iron ore and a smaller but noteworthy decrease in the production of pig iron and steel in the United States in 1911, compared with the production in 1910, due to the large overproduction of ore in 1910, and to a lessening in demand for iron products in 1911. The prospects for 1912 are encouraging, according to Ernest F. Burchard, of the United States Geological Survey, in a report issued last month on the "Production of Iron Ore, Pig Iron and Steel in 1911," but at no time since 1907 has the excessive capacity for manufacturing iron and steel been fully utilized, and nothing short of abnormal activity, which is not likely to occur in 1912, will result in employing the full capacity of the plants.

METHOD FOR THE DETERMINATION OF THE SPECIFIC GRAVITY OF ETHYL ETHER, U. S. P.

The following method for the determination of the specific gravity of ethyl ether was given by George D. Rosengarten, Ph. D. in the November, 1911, issue of the Journal of Industrial & Engineering Chemistry. The method has given satisfactory, practical laboratory results, varying not more than two points in the fourth decimal place.

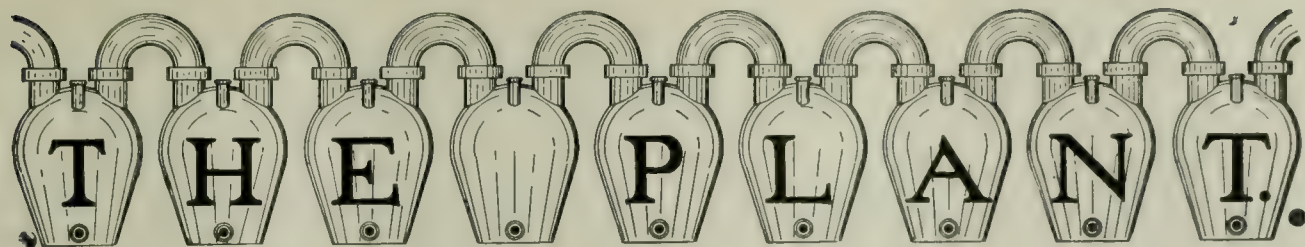
A calibrated pyknometer of 25 cc. capacity, as shown in the sketch, is employed. To determine its volume the pyknometer is first weighed with water at 25° C., choosing a convenient mark on the



Arrangement of CO₂ Absorption Apparatus.

stem, say 30 or 40, whichever may be more convenient, as indicated in the sketch by a line. The pyknometer is then filled with ether to a little above the mark at which the weight of water has been determined and placed in a 1,000 cc. beaker containing water which is carefully kept at 25° C. and constantly stirred with a thermometer. When the volume of ether becomes constant in the pyknometer the excess of ether is drawn off by means of a capillary pipette until the desired mark is exactly reached. The pyknometer is then quickly dried with soft flannel or filter paper and weighed. A capillary pipette for this purpose is easily made by drawing out an ordinary eye-dropper.

The value of the brick, tile, terra cotta, pottery and various other clay products made in California in 1911, according to the United States Geological Survey, was \$4,915,866. This is an increase of \$73,475 over the figures for 1910.



SOME PRESENT DAY ASPECTS OF THE MATCH INDUSTRY.*

By E. G. CLAYTON.

The object of this paper is to summarize the more striking facts connected with the present condition of an industry which has undergone a virtual transformation within the past fifteen years. It is not my purpose to describe in minute detail the processes of manufacture, nor to touch upon the history of matches.

Industrially speaking, here and in many other countries while phosphorus is in match-works a memory only, its reign is over. Match-makers' necrosis in Great Britain is a bad dream of the past. In most countries where white phosphorus matches can still be made, increasingly stringent regulations safeguard the workers. At the instance of public bodies and of manufacturers who have as much regard for the welfare of their operatives as for the accumulation of profits, salutary measures are forced along; and it may be hoped that the goal of universal prohibition will at no distant date be reached. In this matter Denmark led the way, and in the year 1875 forbade the use of matches made with white phosphorus. Switzerland followed in 1879; and since the International Conference at Berne in 1906, the sale and importation of ordinary phosphorus matches have been prohibited by law in France and the French colonies, in Germany, Austria, Italy, Spain, Holland and Dutch India, Switzerland, Luxemburg, and Finland. The agreement between the plenipotentiaries at Berne led in 1908 to the passing by the British Parliament of the White Phosphorus Matches Prohibition Act, and since January 1st, 1910, matches containing white phosphorus have here been forbidden to be imported or sold. They may not be imported into the Australian Commonwealth; and it is probable that Canada will adopt similar legislation. So far, prohibition has not been enforced in Hungary, Belgium, the United States of America, Russia and Japan; but in all these countries, excepting the United States, match works are subject by law to strict regulation and supervision. In America, there is much trouble in connection with the prevention of necrosis. Owing to the very large proportions of white phosphorus used in the manufacture of the American double-tip matches, the operators' risk is considerable; and it is not diminished by the climatal conditions of the country. The humidity

and warmth, which are often greater than in Britain and elsewhere, augment the danger to the workers.

At the hearings in 1910-1911 of the Committee of Ways and Means of the American House of Representatives, interesting evidence was given with reference to the use of white phosphorus and substitutes therefor in the United States and other countries. A bill was introduced in June 1910 "... to provide for a tax upon white phosphorus matches and for other purposes," the main object being "to eliminate through the exercise of the taxing power, the use of white, which includes yellow phosphorus in the manufacture of matches." In the course of the arguments upon this bill it was pointed out that "The United States is left in the unenviable position of permitting the use of a dangerous article in the manufacture of matches, and its position is the more unenviable because a substitute has been found which is entirely innocuous." At a further hearing of the Committee, on January 28th, 1911, the following statement was put in, and submitted by the American Association of Labor Legislation:

"The 'double-dip' match, which is now made in the United States, and rapidly supplanting the old parlor match, generates in the process of manufacture 40 to 50 per cent more poisonous fumes than the parlor match. The regulations in force in foreign countries, prior to the absolute prohibition of the use of white phosphorus, restricted the quantity of poisonous phosphorus to 6 or 7 per cent (in no cases more than 10 per cent.—Denmark) of the match compositions. To-day in the United States the match manufacturers are using from 14 per cent to 20 per cent of poisonous phosphorus in match compositions."

In the light of these and other statements, it is not surprising that Mr. Taft recommended in a message the discouragement and stamping out of the manufacture of white phosphorus products by the imposition of "a heavy Federal tax." It is possible, indeed, that there will be prohibition before very long in the United States and British North America. The probability is the greater in the States, because the workers in America match factories are stated to be confronted by increasingly dangerous conditions of work. The British match works operative was never at any period exposed to phosphorus vapors in a degree approaching that associated with the manufacture of the white phosphorus "double-dip" or "double-tip" match, now so popular in the United States. The readily ingitable, sensitive and softly burning added tip of this product, which in America is said to be

*From the Journal Society of Chemical Industry.

superseding the ordinary paraffin-dipped strike-anywhere match, may contain as much as 20 per cent. or even more, of white phosphorus. Meanwhile, in view of these circumstances, and of the expressed wish of the President of the United States that American labor should be protected from the ravages of necrosis in the same degree that other countries, including Great Britain, have shielded their workers in match factories, the Diamond Match Company last year took an important step. Sole owner of the Letters Patent covering the use of tetra-phosphorus trisulphide in America, the Company on January 27th, 1911, surrendered these for cancellation, so that that compound can freely be used as a substitute for white phosphorus, by any and all match manufacturers within the United States. This action, especially if followed by the taxation of white phosphorus matches, may put an end to the use of white phosphorus in America.

In addition to Great Britain, the chief match manufacturing countries are Sweden and Norway, America, Germany and Austria, China and Japan. In France, the industry is a State monopoly.

British manufacturers in 1907 produced seven hundred and seventy-five thousand pounds' worth of matches, and of this amount nearly one-tenth part was exported. In 1910, about 17¼ million gross of boxes were consumed in the United Kingdom; and about half these were of foreign production. Against these figures may be set those for America, Germany and Austria, Sweden and Norway, and France, for which I am indebted to Mr. G. W. Paton, Managing Director of Messrs. Bryant and May, Limited. Approximately they are:

	Gross of boxes per annum.
Sweden and Norway.....	24,290,000
Germany and Austria.....	14,000,000
France	4,800,000
America	21,800,000

In Japan, the total export is said to have been in 1909 41,407,083 gross; but the competition of Germany, Sweden, and, latterly of China, have since caused very serious injury to the Japanese match trade, and exports have greatly diminished.

The values of the exports of British manufacture to foreign countries and to the Colonies have recently been as shown in Table I.

It is unfortunately too evident that there has been a gradual shrinkage in our foreign trade. Competition is, of course, extremely keen. The imports from foreign countries, during the corresponding period, are shown in Table II.

At one period Great Britain was far behind other countries in regard to the methods of manufacture in use. This is no longer the case. It is due to the enterprise and prescience of the larger British companies and firms that today we can claim to be among the most progressive match-producers of the world. The factories and methods of working in the United Kingdom now challenge comparison with those to be

seen in any other country. At Bow, and Bromley-by-Bow, London, at Liverpool, Gloucester, Manchester, Belfast, Dublin and elsewhere, there are match works provided with plant and machinery second to none in completeness and modernity. The new factories of

TABLE I.—EXPORTS OF BRITISH MATCHES.

		Total to foreign countries. £.	Total to British pos- sessions. £.	Grand Totals. £.
1890	Safety matches and others	16,517	129,366	145,883
1895	Safety matches and others	9,849	77,470	87,319
1900	Safety matches.....	1,175	89,016	8,903
	Other kinds	8,677		89,965
1905	Safety matches.....	1,260	60,232	9,841
	Other kinds.....	4,914		56,565
1908	Safety matches.....	853	81,017	10,703
	Other kinds.....	3,629		74,796
1909	Safety matches.....	1,212	84,752	16,356
	Other kinds.....	3,839		73,447
1910	Safety matches.....	1,626	82,569	14,718
	Other kinds.....	2,270		71,477

Messrs. Bryant and May, at Bow, and their works at Liverpool, are without doubt among the finest in the world.

Abroad, at Tidaholm, Jönköping, Uddevalla and elsewhere in Sweden; at Lattenburg, Rheinaubaden and Vordamm (the Deutsche Zundholzfabriks Aktien-Gesellschaft), at Cassel and Kostheim (Messrs. Stahl and Nölke's), and at Habelschwerdt, Göppingen, Ulm, and Augsburg in Germany; at Aubervilliers, Pantin and Marseilles, in France; at Schuttenhofen, Austria; in Ohio, New York, Michigan and elsewhere in the American States; and in numerous other places in different parts of the world, there are match factories of the first rank, well provided with machinery and other

TABLE II.—BRITISH IMPORTS.

		Total from foreign countries.	Total from British possessions. From Australia.	Grand Totals.
1890	Safeties } Other kinds } (all)	368,886	30	368,916
1895	Safeties } Other kinds } (all)	362,900		362,000
1900	Safeties	203,818		203,818
	Other kinds.....	177,239		177,239
1905	Safeties	263,460		263,460
	Other kinds.....	318,238		318,238
1908	Safeties	327,573		327,573
	Other kinds.....	281,095		281,095
1909	Safeties	341,693		341,693
	Other kinds.....	256,967		256,967
1910	Safeties	306,519		306,519
	Other kinds.....	173,418		173,418

appliances of recent types; and in most of these establishments there are stringent regulations providing for conditions of working favorable to the health of the operatives.

Formerly, for the production of a box of matches at least a dozen separate operations were necessary. Some were effected entirely by hand. Each required some manual labor. The boxes were made, or at least folded and pasted, by hand, in the homes of the workers, and the splints or sticks of wooden matches

were cut by "toothing and flaking" machines from planks or deals, previously smoothed, cross-cut, and steamed. The splints were dried, either on trays in drying rooms, or in heated revolving cylinders, and then filled, at first by very simple machines, into dipping frames or clamps, and later, according to a more elaborate process, into coils of cotton webbing. The coils containing the match-sticks, double the length of a match and with the ends projecting on both sides, were carried by hand to the paraffining tank; and after a preliminary heating on a hot plate, the two ends of the splints were dipped in melted paraffin wax. I say nothing about the antediluvian method known as sulphuring, which was superseded by paraffining. The frames or coils of paraffined splints were conveyed sometimes by a "creeper" to another department called the dipping room, and there by hand in some of the igniting-composition, spread (also by hand) upon the steam-heated top-plate of a dipping table. When both sides of a coilful of splints had been dipped, drying was effected by exposing the coils or frames on racks, in drying rooms maintained at a suitable temperature.

The igniting composition, excepting that for safety matches, invariably contained white phosphorus, which had been stirred into a warm solution of glue and potassium chlorate, to which other constituents, such as powdered glass, "fillers," and coloring agents, were added. The resulting emulsion was then stirred and milled. The dipped and partly dried matches were then "racked out" or "laid out," "halved" by pivoted lever knives, and "boxed," all these operations being carried out by hand, excepting where "unwinding" machines were used, which simultaneously "laid out" and "halved" the two-headed splints as they were released from the coils. During the older process of "halving," and the final operation, "boxing" "firing" often occurred.

The foregoing is a brief summary of the older methods of manufacture; and it can readily be understood how much manual labor was required for these numerous and entirely separate operations.

During the past fifteen years the mode of manufacture has been so changed that to describe it, even superficially, is like giving an account of a new industry. The principles of the manufacture are new; the chief constituents of the igniting compositions have been altered; and even the materials of the match stems are in numerous cases different from those used twenty years ago.

At the present time, the boxes as well as the splints (at all events, the small, or "minik" sized splints), are in the greater factories made new and ingenious labor-saving mechanism. Many of the splints are cut actually in the match-making machines.

Manual labor has been replaced wherever possible by elaborate machinery, automatic, continuous, cleanly and hygienic. Rooms stuffy with the "fume" of partially oxidized phosphorus, or dim with the smoke from fired matches, have given way to spacious and

lofty halls, admirably ventilated, brilliantly lighted, and destitute of odor; and the improved appearance of the workpeople testifies to the betterment of their health and surroundings.

For the production of the common aspen-wood matchboxes and splints, veneers are cut from barked logs by a log-peeling machine, and divided into bands, narrow for splints, wide for boxes. For the last-named, the bands are scored, guillotined, dyed and transferred to boxmaking machines, of which there are two kinds, "inner" machines, for the drawers or "inners" of the boxes, and "outer" machines, for the covers or "outers." These machines fold up, paste, paper-coat, label and deliver on to endless carriers, which convey the covers and drawers to drying rooms. The covers are "sanded," and the drawers are inserted by special machines. For cardboard boxes also, there are "inner" and "outer" machines, the former cutting, scoring, folding, gluing and drying (on a moving chain) the insides of the boxes; the latter cutting, scoring, pasting, folding, printing, gluing, sanding and delivering the outsides, at the rate of about 16 a second.

In making the aspen-wood splints for small-sized matches, narrow but somewhat thicker veneers than those used for the boxes are cut by a log-peeling machine, and guillotined by another machine into rectangular match sticks. These are rendered unflammable by impregnation with ammonium phosphate solution, dried in a revolving cylinder, "cleaned" and straightened in "jogging" appliances, and packed in receptacles, so as to be ready for feeding into the hoppers of the match machines. Splints for the larger matches are cut at present from pinewood, by a different method; but such timber is becoming scarce, and probably aspen-wood will be adopted instead, to a still larger extent than is so far the case.

The match machines are of course the most striking and distinctive features in a modern match works. An endless chain of match-plates, about 230 yards in length and traveling over a series of carrier-wheels, conveys immense numbers of single length rectangular splints, jutting downward from it like the bristles of a scrubbing brush. The splints are at first fed into a hopper, "jogged" and forced by plungers into rows of apertures in the match-plates. The great traveling chain carries the splints, successively, over a hot plate, through a steam heated bath of paraffin wax, then over a dripping roller, partially immersed in a trough of dipping composition, and lastly over all the drums or carrier wheels. This occupies an hour or thereabouts, during which the matches dry. The chain brings them to ejection-plungers in the fore part of the machine, where a box-filling machine places the matches in the drawers of match boxes, inserts the drawers in the covers and transfers the finished boxes to a wrapping machine, which puts up the boxes in dozen packets. One such match machine, attended by eight girls, yields 1,000 gross of boxes per diem, is automatic from beginning

to end, and its production is continuous. This type of machine is used for the manufacture of small and large sized ordinary and safety matches. Certain other forms of automatic and continuous match machines called groove-stick and round-stick machines, punch out their own match splints from blocks of pine-wood fed in near the front of the machine. The cut splints—circular, or nearly so, in section—are conveyed by an endless chain or perforated match-plates over a hot plate, paraffin bath, and the rest, just as in the previous case, returning after the circuit of the carrier-wheels to the front of the machine, where the matches are discharged into the insides of cardboard boxes. These are passed along continuously to an elevated table, at which several seated girls sheath them in the covers. The round-stick and groove-stick machines, it will be seen, literally take in wooden blocks and turn out finished matches; the final part of the “boxing” is the only operation which is not affected automatically. Machines of the types here described require the attention of fifteen operatives, yield about 800 gross of boxes a day, and supply matches of the pine-wood vesta class or the like. Wax vestas are made in wax match machines of very similar construction, but the cut lengths of taper are held by clips or strings in the endless chain, instead of in apertures or perforations; and for obvious reasons there is neither hot plate nor paraffining. The rest of the operations are identical with those previously described.

Machines such as those previously mentioned are used by Messrs. Bryant & May, and in America by the Diamond Match Company; but other automatic machines, constructed upon similar principles, though of very different appearances and capacities, are in use in this country and on the Continent. Roller of Berlin, Sebold of Durlach, the late A. Legerman of Jönköping, Sweden, and Sevene and Cahen, of Paris, may be mentioned among the numerous makers and inventors of automatic match machinery.

In the modern operation of manufacturing strike-anywhere matches, the substitute for white phosphorus mostly adopted in this country, and largely on the Continent, is tetraphosphorus trisulphide, P_4S_3 , the commercial name for which is phosphorus sesquisulphide; but scarlet phosphorus is used in England to a small extent; and, besides dark red, or “amorphous” phosphorus, several varieties of light red phosphorus, preparations of phosphorus and sulphur containing the elements in different proportions from those present in tetraphosphorus trisulphide, phosphorus hydrides, and certain metallic salts of hypophosphorus, thiophosphorus, and hypothiophosphorus acids have in various places been tried or are in use. This list is not by any means exhaustive; but if to the rest be added lead thio-sulphate—very decently-striking matches made with which substance I have had for examination in the laboratory—and various sulphur and thiocyanogen compounds of metals, all the more important latter-day

substitutes for white phosphorus have, it is believed, been named. Dark red phosphorus, commonly called amorphous phosphorus, is still used here and abroad on the rubbers of the boxes for safety matches; and there is nothing particularly new to relate about these. The rubbers of book-matches also contain red phosphorus. I may conveniently conclude the paper with some general remarks on the various kinds of matches. The chief varieties of matches made in this country are square, wood-stemmed, strike-anywhere matches (of two sizes), wood-stemmed vestas, wax-stemmed vestas, wood-stemmed safety matches (of two sizes), and cardboard-stemmed safety matches, or book-matches. Vesuvians are also made, but are obsolescent. Strike-anywhere matches in the latter decades of the nineteenth century constituted over 80 per cent of the matches used by the public, but in 1910 dwindled to under 64 per cent of the total quantity. The popularity of safety matches has correspondingly increased. Wood-stemmed vestas are fast displacing vesuvians, and materially reducing the consumption of wax-stemmed vestas. A manufacturer not long since informed me that whereas some years ago he employed sixty girls daily at the machines for making “braided light” vesuvians, now he has one girl occasionally engaged on such work. The safety match with a cardboard stem, called a book-match, is produced chiefly for exportation, and has but a limited use in this country. It is in one respect an interesting reversion to the earliest type of “fusee,” in that the stem is of cardboard. Cleverly devised little machines print the card, cut teeth in it, tip the teeth in the match composition, fold, stitch into books and paint on the rubbing paste. Lastly the noiselessly and easily struck “double-dip” match, to which allusion has been made, is in the United States an extremely keen competitor of the ordinary strike-anywhere matches, which, by the way, are usually called in America “parlor” matches; but whether the double-dip match, in its present form, can continue to be made in the face of the agitation against the use of white phosphorus, remains to be seen.

In 1911, according to the United States Geological Survey, 2,390 ounces of palladium were produced, 300 ounces from crude foreign and domestic sands and the rest from the refining of copper ores and copper bullion. Palladium finds a fairly large use in technology. Circles of astronomical instruments are made of it, and it is also employed in watchmaking. Its most extensive use is probably for certain alloys in dental work. It is also employed for soldering platinum metals. As it is not altered or discolored by exposure to air it is often used for plating metal ware. The demand for this metal is greater than the supply. According to the Bureau of Statistics, 1,218 troy ounces of palladium were imported into the United States in 1911, the value assigned being \$56,307, or \$46.22 an ounce.

ENAMELS FOR SHEET STEEL.*

By ROBERT D. LANDRUM.

Enamels for sheet steel are boro-silicates of sodium, potassium, calcium and aluminum and are, in every sense of the word, glasses. Such enamels are so compounded that they form a homogeneous, glossy coating on the surface of the sheet steel utensils, which will not be corroded by the acids or alkalies used in cooking and which will resist punishment both by impact and by rapid changes of temperature.

Although an enamel is a glass, the fact that it must adhere to steel and resist the abuse common to cooking utensils makes necessary the addition of other ingredients besides those used in manufacturing ordinary glass. In enamels, ground quartz, flint or sand supply the silica, and feldspar and clay, the alumina. Fluorspar or calcite is added to supply the lime and cryolite to render the enamel translucent. Soda ash and pearl ash are fluxes adding sodium oxide or potassium oxide to the product, and borax furnishes the boric anhydride, which adds many desirable qualities, such as greater ductility and elasticity. Sodium or potassium nitrate is used in white enamels and manganese dioxide in dark colored enamels as an oxidizing agent. Oxide of cobalt is used in enamels which come directly in contact with the steel and adds adhesiveness to this coating.

For producing white enamels, oxide of tin is used; for blue, cobalt; for violet and brown, manganese; for gray, nickel; for green, copper or chromium; for yellow, uranium or titanium; and for red, iron, selenium or gold.

Enameling is still held as a secret art, and the formulas are carefully guarded. Most companies allow very few visitors to go through their plants and some keep their employes in ignorance by various schemes. In one American works, each of the enamel raw-materials is given a number. They are ordered, shipped, kept account of, and stored under their respective numbers, and only those in authority even know what materials are used. In this same factory, employes of one department are not allowed in another and after being employed in one department, a man is barred from employment in any other. Some works have the formula for each enamel divided into two parts, one of which is mixed by one man, the other by a second, and certain proportions of each are then mixed together by a third man. In practically all enameling works, the materials are weighed on a scale, the beam of which is hidden from the laborers, who are also generally of foreign birth and are changed frequently.

The sheet steel which is used for enameled ware is as nearly as is possible free from carbon, silicon, sulphur and phosphorus, and its manganese content is

generally about 0.2 per cent. These sheets come in squares and oblongs from 27 to 20 gauge and are circled, stamped and spun with as little heat treatment as possible and with the use of a lubricant that can easily be cleaned off. The ears, handles and other trimmings are, as far as is practical, welded on, as riveted joints are difficult to enamel.

The surfaces of the completed steel vessels are thoroughly freed from carbonaceous matter by annealing at a low red-heat and are then pickled in hot dilute acid, thoroughly rinsed in water, and then in weak alkali solution. After a quick drying they are ready to be enameled.

In the making of an enamel, the various raw-materials are loaded from their respective bins into small cars called "dollies." These are filled to a line which approximates the correct weight, then they are pulled on a scale, the beam of which is hidden from the workman, and the enamel-master indicates whether the load is light or heavy, and the workmen correct this by shoveling on more or taking some off. When each of the "dollies" is corrected so that the required amount of material for a mix is in it, all are dumped on a large, hard maple floor, the coarser material on the bottom and the finer on the top. This pile is thoroughly mixed by shoveling, and is loaded into an electric elevator, which hoists it to its bin. There is a bin for each different kind of enamel, and a traveling bucket which holds a melt (about 1,200 lbs.) carries the mix to the tank furnaces where it is melted into a liquid glass.

These tank furnaces are regenerative, reverberatory furnaces like those used in the manufacture of glass, and natural gas or crude oil is an ideal fuel for them. However, in the older enameling works, coal is used directly, and in the later ones producer-gas is used as a fuel. The temperature required for smelting the different enamels varies from 1,000° C. for a glaze to 1,300° C. for a ground coat, and, in most enameling works, pyrometers are installed to assist in controlling these temperatures. Each furnace will give seven or eight melts in 24 hours.

After the enamel is melted into a liquid glass, a fire-clay plug in the front of the furnace is pulled out and the glowing liquid stream plunges out and is caught in a tank of cold running water. The reaction is terrific and the glass mass is torn and shredded, cracking into small pieces like popcorn, each of which is a myriad of microscopic seams and fissures. This "quenching," as the process is called, toughens the enamel and facilitates the process of grinding which comes next.

The water is drained from the tanks, leaving the "enamel frit." This is shoveled into pans (a certain weight to a pan) and is ready for grinding.

In the mill room, the enamel frit is ground in large ball mills for about 30 hours. These mills are cylindrical, about 5 ft. long and 6 ft. in diameter, and are lined with porcelain bricks. The frit is put into them

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with 50 per cent of water and several per cent of white ball-clay. For the white cover-coat enamels, tin oxide is also added. The mill revolves and the constant impact of the flint stones against the glass particles grinds them to an impalpable powder, which mixes with the water and the clay, forming a mass which has the consistency of rich cream. This is loaded into tanks, where it is allowed to age a week or so.

From the mill room the enamel is taken to the dipping room, where it is put into tanks that are like large dish-pans. These are sunk into tables, and at each tank a slusher works. The slusher takes the stamped-out steel vessel, which has been thoroughly cleaned, and plunges it into the enamel. When taken out, the wet enamel forms a thin film over the entire surface. By a gentle swinging motion, the excess of enamel is thrown off, and the vessel is placed bottom down on three metal points projecting from a board. Three or four vessels are put on a board; these are placed on racks and when the vessels are thoroughly dry they are carried to the furnace room.

The furnace room contains a long bank of muffle-furnaces and in these the ware is put after drying. The temperature in these furnaces is about 1,000° C. and here the little powdered particles of enamel are fused together in a solid glass coating over the vessel, the process requiring from three to five minutes.

Each coat is burned separately. For instance, we have a pudding pan that is to be a three-coat white inside, turquoise-blue mottle outside. It is first dipped in the ground coat enamel, the excess is shaken off and the vessel put on a three-pointed rack and dried. After drying, the enamel stands in little grains all over the surface of the ware, adhering to the metal on account of the raw clay ground with it. At this stage every care must be taken, for a scraping, even of the finger nail, would take off some of the powdered particles of the enamel. This pan is then put into the muffle of the furnace, and the heat fuses all the little particles together, leaving a tight-holding vitreous coating all over the surface of the vessel. This fundamental coating is nearly black, due to the oxides of cobalt and nickel which it contains, and shines with a glass-like luster.

After the vessel has cooled at the ordinary temperature of the room, it is again brought to the slushing room, and here is covered with an enamel—this time a

white. It goes through the same process as before, except that a black bead is brushed around the rim. On account of the dark color of the first coat showing through, this second coat, after it is burned, has a gray appearance, and is called the "gray coat" or "first white." The vessel is again sent to the slushing room, and is dipped into a white enamel, the excess shaken off, and before drying the blue-green enamel is sprayed on the outside.

This spraying process was at one time done by dipping a wire brush into the wet blue-green enamel and the slusher shaking it over the surface of the vessel, causing the blue enamel to fall in little speckles all over the white enamel. In most factories, however, spraying machines, which work on the principle of an atomizer, have been installed. A tank full of the colored enamel stands over the table and the enamel is forced out through a nozzle in a spray by compressed air. The flowing of the enamel is controlled by the foot of the slusher as he holds the vessel in the spray. The vessel is then dried and the coating is fused in the muffle-furnace, the result being turquoise-blue spots on a white background.

The finished ware is assorted into three lots; firsts, seconds, and job lots. Some of the seconds and job lots are fit for redipping. They may have some little spots where the original vessel was not properly cleaned and where, on account of the rust or dirt, the enamel did not adhere. These spots are filed or are held under a sand-blast until the exposed surface is perfectly clean, and then the vessel is covered with another coat of enamel.

There are schemes for saving money in all manufacturing plants, and in the enameling business a large part of the profit comes from the residues. For instance, every bit of enamel is scraped from the tanks and tables, all sweepings from floors are saved, and all the waste water from the various departments is first carried into catch basins, and every few days these are cleaned and the residue, which has settled to the bottom, is taken out. The residues from all these sources are again melted with the proper amount of fluxing material and coloring matter, and this dark-colored enamel is used for coating the cheaper wares.

In order to give an idea of the composition of a white cover-coat frit, such as is used on cooking utensils, and to show the method used by ceramists to calculate its so-called molecular formula, the following

Batch mix. Material.	THE ENAMEL. ²									
	Per cent used.	M.W. equivalent. ³	Na ₂ O.	K ₂ O.	CaO.	MgO.	Al ₂ O ₃ .	SiO ₂ .	B ₂ O ₃ .	F ₂ .
Feldspar	38.6	602	0.0641	0.0288	0.0250	0.0038	..	0.0641	0.4558	..
Quartz	19.0	60	0.3167	..	..	..	..	0.3167	..	..
Borax	15.4	382	0.0403	0.0403	..	..	..	..	0.0806	..
Cryolite	11.7	420	0.0279	0.0837	..	..	0.0279	..	..	0.1674
Saltpeter	6.5	202	0.0322	..	0.0322	..	..	..	..	..
Calcite	6.5	100	0.0650	..	0.0650	..	..	..	..	..
Fluorspar	1.3	78	0.0167	..	0.0167	..	..	..	..	0.0167
Magnesium carbonate.....	1.0	84	0.0119	..	..	0.0119	..	..	..	..
Total			0.1528	0.0572	0.0855	0.0119	0.0920	0.7725	0.0806	0.1841

¹P. 18. Published by Keramische Rundschau, Berlin, N. W., 21.

²A complete description of the manufacturing of this enamel by the writer in "A Comparison of Ten White Enamels" in the

³Molecular equivalent equals per cent used divided by M. W.

and of the physical properties of a ware coated with it is given Trans. Am. Ceramic Soc., Vol. XIV.

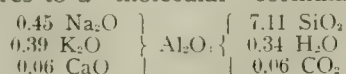
enamel, the formula of which is taken from the 1911 edition of the "Taschenbuch für Keramiker," is used:

Feldspar 38.6 per cent, quartz 19.0 per cent, borax 15.4 per cent, cryolite 11.7 per cent, saltpeter 6.5 per cent, calcite 6.5 per cent, fluorspar 1.3 per cent and magnesium carbonate 1.0 per cent.

All the materials used were practically pure except the feldspar, which was a pegmatite of the following composition:

	Per cent.
Silica.....(SiO_2)	70.66
Alumina..... Al_2O_3	16.85
Potassium oxide..... K_2O	5.93
Sodium oxide..... Na_2O	4.61
Lime..... CaO	0.52
Carbon dioxide..... CO_2	0.41
Moisture..... H_2O	1.02

This figures to a "molecular" formula of

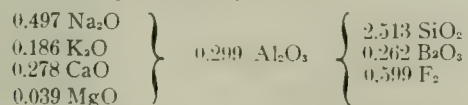


the molecular weight of which would be 602.

The other materials used were:

Material.	Formula.	Equivalent weight.
Quartz	SiO_2	60
Borax	$\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$	382
Cryolite	$2\text{Na}_3\text{AlF}_6$, giving $3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{F}_2$	420
Saltpeter	$2\text{K}_2\text{O} \cdot \text{N}_2\text{O}_5$	202
Calcite	$\text{CaO} \cdot \text{CO}_2$	100
Fluorspar	CaF_2 , giving $\text{CaO} \cdot \text{F}_2$	78
Magnesium carbonate	$\text{MgO} \cdot \text{CO}_2$	84
Feldspar	(Given above)	602

The above total corresponds to the following molecular formula of enamel:



A U. S. Consular report quotes from the Frankfurter Zeitung as follows with respect to a new method of galvanizing iron: In order to protect iron objects from rust, it is customary to coat them with zinc either electrolytically or by plunging them in a bath of melted zinc after careful cleansing. The disadvantage of these methods is that a real fusion of the two metals is not obtained. As a result the zinc coating is likely to be attacked by the atmosphere. This may be avoided by a recently patented process which consists in so preparing the iron that the zinc gets into its pores. After steeping in sulphuric acid the iron is placed in a solution of mercury chloride and then heated, resulting in decomposition of the mercury chloride and precipitation of metallic mercury, which forms an amalgam with the iron on the surface. The iron is then plunged into a zinc bath heated to 500° , where it remains three minutes. Iron galvanized by this process shows unusually strong adhesion of coating to metal. Microscopic investigation shows that the zinc penetrates into the pores of the iron, and in case a portion of the coating is worn or broken off, iron does not rust owing to the presence of sufficient zinc in the pores.

SOYA BEAN OIL FOR PAINT PURPOSES.*

By MAXIMILIAN TOCH.

From 1890 to 1909, the price of linseed oil fluctuated between 30 cents and 50 cents per gallon. On a few occasions the prices were higher, but a fair average for the 19 years was 40 cents per gallon, although in 1896 it went as low as 25 cents. Towards the end of 1909 it rose from 60 cents to 68 cents within two months, and in September, 1910 it reached \$1.01 per gallon. Since that time it has been fluctuating between that price and 75 cents. Owing to the high price of linseed oil in 1910, many painting operations were deferred, awaiting a lower price, or inferior material was used in place of linseed oil.

The value of menhaden fish oil had already been recognized and while it is admitted that fish oil replaces linseed oil for many purposes, it is by no means a true substitute. The principal use, however, for fish oil today is in the manufacture of linoleum, printing inks, and certain paints which are exposed either to the hot sun, or on hot surfaces.

In 1909 soya bean oil as a paint oil was practically unknown. Since that time many investigators have published more or less conflicting articles concerning soya bean oil, and even the physical and chemical constants of soya bean oil vary to some extent. Owing to the fact that discordant results were continually obtained, it is only within the last year that it has been possible to state with some degree of certainty whether soya bean oil is a substitute for linseed oil, an adjunct to it, or neither. The reason for this uncertainty and discrepancy is apparent when it is stated that the author himself has experimented with 33 different varieties of soya beans, and in the records of the Department of Agriculture at Washington no less than 280 varieties of soya beans are listed.

From time immemorial, the soya bean has been grown in China and Japan, where it has served as one of the staple articles of food, and as the basis for a number of food preparations. In Europe and the United States, however, the value and uses of the bean have been but little appreciated until very recently (1908) when, on account of the scarcity in the cotton seed supply of the world, soap and glycerin manufacturers began to turn their attention to its possibilities. In Manchuria, where by far the major portion of the soya beans are grown, practically the entire crop is available for export. The following figures taken from the Consular Reports will serve to show the extent of the soya bean industry during the past three years:

	Tons. 1909.	Tons. 1910.	Tons. 1911.
Total shipments of beans from			
Far East.....	1,470,870	1,200,000	1,500,000
Imported into Europe.....	400,000	500,000	340,000

As above statistics indicate, China and Japan retain for domestic consumption practically two-thirds of the

*From the Journal Society of Chemical Industry.

available supply of beans. The sugar plantations in Southern China and the rice fields of Japan annually consume enormous quantities of soya beans and bean cake as fertilizer, while the extracted oil is used as food by the natives.

In connection with the use of soya beans and soya bean oil for edible purposes, it may be mentioned that there has been re-established at Les Valleees, France, a thoroughly up-to-date factory for the production of a wide assortment of food products from soya beans. Among the more important of these may be mentioned: Milk, cheese, casein, oil, jellies, flour, bread, biscuits, cakes and sauces. According to Dr. G. Brooke, Port Health Officer of Singapore, the soya bean, more nearly than any other known animal or vegetable food, contains all the essential and properly proportioned ingredients of a perfect diet.

All soya beans are leguminous plants, which do not tend to deplete the soil of nitrogen, for the typical soya bean plant is self-nitrifying and grows in almost any soil that contains a reasonable amount of potash. In addition to this, the soya bean enriches even very poor ground when used as a ground manure. This is done by planting the seed promiscuously, allowing it to grow to a height of about 6 inches and then turning it in. In this way both nitrogen and potash are given to the soil for future use in an available form. The average height of the soya bean plant is about 26 inches. The pods resemble those of our sweet pea. They are about $2\frac{1}{2}$ inches in length and are covered with a hairy growth. Generally there are two or three beans in each pod. After the oil is extracted from the bean, the cake appears to be very valuable as a cattle food, while the leaves and stalks, if collected and set in a dry place, make excellent silage. We thus have practically the entire plant available for use, with the exception of the roots.

The average composition of the soya bean varies within fairly narrow limits among the different varieties of soya beans. In the table are listed the analyses of a few of the varieties of soya beans:

TABLE I.

Variety.	Water, Pct.	Protein, Pct.	Fat, Pct.	Nitrogen, free extract, Pct.	Fibre, Pct.	Ash, Pct.
Austin	8.67	36.50	20.55	24.41	4.00	5.78
Ito San	7.42	34.66	19.19	27.61	5.15	5.97
Kingston	7.45	36.24	18.96	26.28	4.79	6.28
Mammoth	7.49	32.99	21.03	29.36	4.12	5.01
Guelph	7.43	33.96	22.72	25.47	4.57	5.85
Med. yellow...	8.00	35.54	19.78	26.30	4.53	5.85
Samarow	7.43	37.82	20.23	23.65	5.05	5.82

When the author obtained discordant results from the soya bean oil then on the market, the first impression was that the oil might have been adulterated, but this did not prove to be the case. The oil was, in all cases, pure soya bean oil, but from a seed which was not particularly adapted for making a paint oil. Through the U. S. Department of Agriculture many varieties of seeds were received, and through the various seed dealers in the United States, quantities of seeds of all kinds were purchased. The method of ex-

traction followed was to grind the seeds very finely in a mill and digest with gasoline in the cold. The solvent was then evaporated and the oil recovered. Without going into any lengthy details, the percentage of oil extracted averaged 18 per cent, and although soya beans range in color from a cream white to a jet black, it must be noted here that all the oils extracted from the various seeds were paler than finely pressed linseed oil, and none of them showed the chlorophyll extract as markedly as fresh flaxseed. On obtaining the various samples of oil, it became evident why the discordant results were obtained, for some of them dried within a reasonable time and some did not.

It has been stated that soya bean oil is not as pale as raw linseed oil and belongs to the semi-drying class of oils. I must correct this statement; soya bean oils made from cold pressed seeds such as haberlandt, Austin, Habaro, Ebony, Meyer, and Ito San give excellent results and have a specific gravity as high as 0.926 with a yield ranging from 16 to 19 per cent. Furthermore, a drier made from red lead or litharge is unsuited for soya bean oil, but a tungate drier, which is a mixture of a fused and a precipitated lead and manganese salt of china wood oil and rosin, acts on soya bean oil, exactly the same as a lead and manganese drier acts on linseed oil. In other words, a fairly hard, resistant and perfectly dry film is obtained by the addition of from 5 to 7 per cent of this drier, within 24 hours. Soya bean oil, and when I mention this name hereafter, I refer only to that suitable for paint purposes, is the nearest oil we have to linseed, and under the proper impetus of the Department of Agriculture much of our waste and unproductive land between Maryland and Georgia, and from the Coast to the Mississippi, will yield productive and profitable crops. The only drawback to the planting of soya bean is the fact that it needs much water. In 1911, many of the experimental plantings failed on account of the drought which was prevalent in the United States, but in low marsh land this plant ought to yield a profitable crop. It is doubtful whether the soya bean would grow profitably in the extreme South. In Cuba the cow-pea, which is analogous to the soya bean, will sometimes grow to a height of 20 feet, and form a thick matt around the base or abutment of a railroad bridge, and that within a few months. This would indicate that a soil would have to be selected where the bean would not grow to a height greater than 5 feet, otherwise the stalks would be too thick and it would be difficult to harvest it. Farmers' Bulletin No. 372 of the Department of Agriculture, makes the statement that 20 lb. of seeds are required to the acre, and that the production is from 25 to 40 bushels, each bushel weighing 40 lb. If this is a fact, and since little or no fertilizer is needed, and when fertilizer is needed a preliminary crop can be grown and turned in to form its own fertilizer, the American farmer should be encouraged to try this crop. Furthermore, in Kentucky two crops during the summer

can be grown, for some of the soya beans that have been tried there have ripened early, and the second crop has ripened late, two different selections of seed having been used. The statement has been made that soya beans could not be harvested properly in this country on account of the high cost of labor as compared with that of Manchuria and Japan, but this is evidently erroneous, in view of the fact that enormous quantities of beans are grown in Minnesota for food purposes and harvested by machinery. Even in Manchuria the beans are allowed to dry and then thrashed out by means of horse power. At any rate, if we have any difficulties now with the harvesting of a new kind of crop, it is safe to assume that with the American inventive genius in harvesting machinery appliances will be invented which will overcome this, for the soya business has no greater harvesting difficulties than the edible bean.

Soya bean oil appears to consist of from 94 to 95 per cent of glycerol esters. Of these 15 per cent are saturated acids, such as palmitic acid, and 80 per cent are liquid unsaturated fatty acids containing 70 per cent oleic acid, 24 per cent linolic acid and 6 per cent linolenic acid. The iodine number of soya bean oil has been given as ranging from 121 to 124, but the Manchurian cold pressed oil will average as high as 133.

It may be of interest to show a comparative table here, Table II, between the physical and chemical constants of soya bean oil of known origin like Manchurian cold pressed oil as compared with linseed oil:

TABLE II.—SOYA BEAN OILS.

Name.	Color of seed.	Color of oil.	Sp. gr. 15 C.	Acid value.	Iodine value.
Meyer.	Brown.		0.9264	0.44	127.0
Peking.	Black.		0.9279	0.14	135.4
Haberlandt.	{ Straw-yellow.	Extremely pale.	0.9244	0.00	129.8
Farnham.	{ Straw-yellow.		0.9234	0.65	131.8
Taha	{ Black.	Pale amber	0.9248	0.16	127.0
	{ Olive.	somewhat deeper	0.9222	0.47	118.2
	{ Saddle.	than above.			
Mammoth.	{ Straw-yellow.		0.9248	0.17	129.3
Edward.	{ Brown.		0.9257	0.14	124.6
	{ Straw-yellow.	Med. amber.			
Shanghai.	Black.	Same depth as previous olive tone.	0.9241	0.63	127.8
Refined linseed oil.....			0.933	1.0	180.1

The specific gravity determinations were made with the pyrometer. The iodine values were obtained in accordance with Hubl's method. The iodine values indicated are somewhat lower than those of cold pressed Manchurian bean oil. This is no doubt to be ascribed to the circumstance that the solvent with which the oil was extracted was driven off by evaporation in open vessels on the water bath, so that the oil became slightly oxidized.

Soya bean oil which is suitable for paint purposes has two characteristics which enable the chemist to determine whether this oil is suitable or not. In the first place, soya bean oil, when heated up to 500° F.,

for a few minutes will bleach, and remain bleached. Some samples which the author has examined have turned almost water white. Linseed oil has this characteristic, but not to the same degree. Cold pressed soya bean oil made from the samples indicated in the previous table, when heated to 500° F., and blown with dry air for from 5 to 7 hours, thickens exactly the same as linseed oil, and attains a gravity of 0.960 or over. This is the surest indication that the soya bean oil which will thicken under these conditions and remain pale is suitable for paint purposes. This thickened oil has excellent qualities and advantages for making what we call in this country "baking japans," and what is known in England as "stoving varnishes."

A sample of standard cold pressed Manchurian bean oil was heated to 500° F. and blown vigorously for 7 hours after cooling to 300° F. The following results were obtained:

	60° F.	Acid value.	Iodine value (Wijs.)
Original oil.....	0.929	2.6	133.6
Blown oil.....	0.963	1.9	105.3

It is interesting to note that the acid value was reduced by blowing. The blown oil dried in 3½ days, whereas the original sample required from 5 to 6 days.

It appears that the varnish made from a suitable soya bean oil bakes to a very hard degree, and retains an abnormal flexibility. As regards the wearing quality of pure soya bean oil compared with pure linseed oil for paint, the author has had somewhat less than three years' experience, and can only say that it is not quite as good as that of linseed oil. A 2-year exposure on a 100-foot fence gave slightly better results for the linseed oil as to hardness and less gloss for the soya bean oil, but a mixture of half soya bean and half linseed oil showed approximately the same results, while a varnish made of 25 per cent of China wood oil with 75 per cent soya bean oil gave equally hard results as linseed oil. It is too soon to prognosticate the value of soya bean oil for exterior painting, but for interior painting soya bean oil is the equal in every respect to linseed oil, and particularly when treated with a tungate drier. Cobalt drier will, under many circumstances, dry even those soya bean oils which are not suited for paint purposes, but for the present cobalt drier is rather too expensive. It has been stated that from 1 to 1½ per cent cobalt drier will dry soya bean oil and fish oil. This is practically true, but 5 per cent is really needed to get the proper drying within 24 hours. Cobalt Tox Tungate is probably the ideal drier for soya bean and fish oils.

This drier, when present in soya bean oil to the extent of from 5 to 7 per cent, will dry the latter within 12 hours.

It is, of course, possible to determine and differentiate a mixture of raw soya bean oil and raw linseed oil for the iodine values and specific gravities are good indications, but when 25 per cent of soya bean oil is added to a mixed paint, neither the author nor anyone in his laboratory can, in all instances, detect its presence.

Blown and thickened soya bean oil is already used by a number of the linoleum and table oil cloth manufacturers, and for printing ink purposes it presents some advantages. For the manufacture of enamel paints, heavy bodied soya bean oil produces most beautiful results, and as perhaps 95 per cent of all enamel paints are used for interior decorative or protective purposes, in this country its use should be encouraged.

It is not within the province of the writer to forecast the future of any paint oil, but there is no doubt that if a campaign of education be urged among the farmers, particularly in those states where soil has been regarded as unproductive, and the proper selected seeds of soya beans are planted, no scarcity in the flax-seed crop will ever again be a menace to the paint and varnish industries. At the time of writing linseed oil is quoted at 75 cents per gallon and soya bean oil at 55 cents per gallon. As soon as thousands of acres shall have been planted with soya beans, the proper machinery installed, and the sale for the cake and the silage arranged, soya bean oil will sell at from 25 to 35 cents per gallon, and after the ground has been productive of soya beans for some time, it will be fit for the growing of even the most difficult crops.

It is estimated that the total European production of glycerine is between 80,000 and 90,000 tons. In 1910 the exports to the United States amounted to perhaps 20,000 tons and in 1911 to about 18,000 tons. Up to July 1, 1912, the exports to the United States this year have amounted to only about 4,000 tons. The belief has been confirmed that the supply of glycerine exceeded the demand during 1910 and 1911, and that American importers bought considerably more than was necessary for use in the manufacture of explosives utilized in the construction of tunnels, railways, and other similar works. In Europe, also, there has been a marked decrease in the sale of glycerine owing to various causes. Since January 1, 1910, the Simplon Tunnel has been completed, a work which absorbed large quantities of glycerine, and there has been considerable diminution in the demand from Switzerland, where glycerine is used largely also for tunneling purposes. Furthermore, the glycerine market has been depressed by the successful introduction of explosives less dangerous than those in which glycerine is used so largely, chiefly nitrate of ammonia, which is manufactured principally in Norway. It is estimated that 30 per cent of the total consumption of explosives is now represented by the so-called safety explosives.

The value of the brick, tile, terra cotta, pottery and various other clay products made in New York in 1911, according to the United States Geological Survey, was \$10,184,376. This is a decrease of \$1,687,573 as compared with the figures for 1910.

NITRATE DEPOSITS.

Nitrate of soda and nitrate of potash were imported into the United States in 1911 to the value of \$17,117,068, according to the Bureau of Statistics. Nearly all the nitrate imported comes from Chile and is used for fertilizing. This enormous expenditure for imported nitrates lends interest to a pamphlet just issued by the United States Geological Survey—"Nitrate Deposits," by Hoyt S. Gale (Bulletin 523). All the known occurrences of nitrate deposits in the United States are described by Mr. Gale, and though most of these are probably in the nature of "prospects" they are interesting and of importance as indicating the possible origin of deposits which can be mined commercially. Last year George Otis Smith, Director of the Survey, and A. H. Brooks, in company with Mr. Gale, visited a reported deposit near Gerlach, Nev., where specimens of salt running high in potassium nitrate were obtained. Reference is made in the bulletin to areas in most of the Western States, where discoveries of these nitrates have been reported from time to time. The extreme solubility of nitrate salts renders it unlikely that concentrated deposits will remain anywhere except in places either not subject to or protected from the solvent action of rain, surface water, or moving ground water. Thus nitrate salts are found chiefly in caverns or caves, or under overhanging ledges, or, as in the Chilean and other South American occurrences, in a region of exceptional aridity. The assertion that none of the nitrate deposits of the character mentioned will prove commercially workable is, according to Mr. Gale, not warranted. Such deposits have proved to be of value under exceptional conditions, as when they were utilized for the manufacture of gunpowder, during war times, in the Eastern States; and it is entirely possible that changing conditions may render some of the western deposits valuable. It must be recognized, however, that so far as may be judged from present evidence, few if any of the deposits now known warrant much outlay for development as a source of commercial nitrate salts.

While the United States is rich in peat deposits, the amount produced is small, that for 1911 being only 64,165 short tons, valued at \$311,486 according to figures compiled by Charles A. Davis and just made public by the United States Geological Survey. By far the greater part of this production was used in the fertilizer industry, 51,733 tons being utilized for that purpose. In 1911 there was a growing consumption of peat for miscellaneous uses, the most important of which seems to have been the use as an absorbent for refuse beet sugar and other molasses, so that these excellent feeding materials can be fed economically to cattle and other live stock. Charred dried peat is also used in poultry food and other commercial foods for stock.

METALLURGY.

FOUNDRY TESTS AND FOUNDRY PRACTICE.*

By W. R. DEAN.

With the advent of the chemical engineer into the brass founding industry and the use of more brass and bronze castings by the mechanical engineers, the foundryman of today has to look after the quality of his metal if he wishes to keep in the field. The foundry foreman has enough to do to look after his production while the chemical engineer looks after the development of the alloys, etc. In the last few years more thought has been given to the alloying and melting of metals and all up-to-date foundries keep in touch with some chemist or engineer. In large manufacturing plants, where a large amount of borings, etc., are made, it is almost impossible to keep the different metals separate, for instance, different kinds of composition turnings may be mixed up by the machine hand unintentionally and returned to the foundryman for him to use as best he can. By the aid of a chemist these could be melted and run into ingots and the chemical composition of the mass determined and used accordingly.

The man in charge of the chemical laboratory of a manufacturing plant should be a chemical engineer, and not merely a chemist, he should be able to make mechanical tests as well as chemical, be able to chart his results for future reference and to draw conclusions from them. A year or two of actual foundry practice will do him no harm and worlds of good. For often what looks good theoretically works out quite differently in actual practice. Take manganese bronze, for instance, you can weigh out two or more heats of this alloy very carefully and on testing have quite different results, due to different conditions in the working of the furnaces and furnace tenders, etc. Theoretically two or more tests of metal of the same composition from different pots should test alike, but they do not. Even in the case of government bronze (88-10-2), tests of which I will speak later, will show different results even when chemical analysis shows the different castings to be the same in composition.

In manganese bronze the tests are controlled better by being sure that the pots of metal are practically of the same composition when poured. That is, that zinc is added to replace the zinc oxidized. To have two or more pots the same or have one pot show the proper grain, at the plant with which I am connected, we carry out preliminary tests before pouring for rou-

tine control. This is done by breaking a "test" with a sledge. In weighing out the copper and zinc for manganese bronze no matter how careful you are, the grain will often vary considerably, and the tests will also vary, for example:

	Tensile strength. lbs.	Elastic limit. lbs.	Elongation in 2 in. %
No. 1.....	73,000	40,000	26
No. 2.....	76,000	34,000	24
No. 3.....	69,000	40,000	25
No. 4.....	80,000	30,000	20

If preliminary tests are taken and the grain kept the same in all cases, as near as possible with the trained eye, the results of the test pieces will be nearer alike. For example, we poured two test pieces from a heat for four different days, breaking one from each heat and keeping the grain the same; the four saved were pulled and gave the following results:

	Tensile strength. lbs.	Elastic limit. lbs.	Elongation in 2 in. %
No. 1.....	72,000	44,000	26
No. 2.....	72,200	44,500	25
No. 3.....	73,000	43,000	25
No. 4.....	72,000	44,000	27

Of course a certain amount of oxidation takes place that is uncontrollable, which is shown by the slight variance, but, on the whole, it is better than the ones not tested.

In alloying a pot of bronze it is a good plan to leave out a small piece of zinc, say 2 or 3 pounds, until you have broken your test bar and noted the grain, for sometimes the grain is a little coarse if all the charge is put in at once, due to the scales or the man weighing not being accurate, or due to other causes. Nine out of ten times the grain will be all right, but the 10th time it will be a little under or a little over. Then it requires that either part or all of the zinc left out should be put in, or if over-grained a small piece of copper, and another test made. The leaving out of the piece of zinc is very beneficial when alloying two or more pots and trying for the same grain.

In alloying two or more pots no matter how careful you are in weighing, melting, etc., the grain of the different pots will differ considerably a good many times, and then the tests will show up this difference so the zinc can be added or not; depending on the grain wanted. It is easier to add zinc than to add copper. It is necessary while consuming the time in trying the tests to keep the pots well covered with charcoal so as not to oxidize, and it is well to throw in a handful of salt. This testing takes from 10 to 15 minutes, according to the number of tests necessary. Don't hurry the cooling of your tests by quenching in water too soon after pouring, and when you do quench do it carefully. That is, plunge it in and out quickly

*Paper presented at the annual meeting of the American Institute of Metals, Sept. 24th to 27th, 1912, Buffalo, N. Y.

and let remain out a few minutes before putting it in again. In this way you will not alter the grain any. Sudden cooling makes the grain coarser.

Different specifications call for different grains; for instance, you might have a specification calling for 65,000 tensile strength, 40 per cent of tensile strength for elastic limit and 25 per cent elongation, or you might have 65,000 tensile strength—30,000 elastic limit and 20 per cent elongation. The latter specification calls for lower elastic limit and elongation but the same tensile strength. For these Matthiessen and Hegeler spelter could be used and run a fairly coarse grain as our elongation is not high and that will ensure our tensile strength being right. For the first use a better spelter, as a higher elongation is called for. Matthiessen and Hegeler spelter might give this tensile strength a good many times, but it is uncertain, depending on the melter. The grain should not be too coarse, as the elongation must reach 25 per cent, which is fairly high. In making the preliminary tests the grain should be coarser than what we expect to get in our test price attached to the casting. It should just begin to show a large crystalline fracture to give about 20 per cent elongation. This preliminary testing is necessary to keep to a standard fracture on account of zinc being so volatile.

If you are using a furnace where the zinc can volatilize easily, as the reverberatory or air furnace, or an open flame furnace, this testing is necessary to keep the grain where it belongs. Often when the melt is waiting for the mold, 2 or 3 pounds of zinc to the 100 pounds of metal is necessary to keep the grain where you wish it. If you are ready to pour when the right temperature is reached, this addition is unnecessary. For our air furnace we leave out 2 slabs for a large heat (60 or 70 hundred pounds) and make a test. Sometimes the grain has been coarse enough with only one slab added and sometimes it has taken all and one or two pounds more to the hundred to get the required grain. For elongation of only 20 per cent we run a coarser grain than for an elongation of 25 per cent.

In getting the grain for the preliminary test it must be coarser than what is wanted in the machine test. For 20 per cent elongation we have the grain a little on the crystalline side, for in the test on the casting it comes finer and the test pulls all right. A little experimenting and testing will give you the grain you wish. When using scrap this testing gives an idea of the amount of zinc to use to get the proper grain. Some allowance must be given for the temperature when adding the zinc. If the melt is extra hot the amount of zinc can be a little more than otherwise to allow for zinc burning out. It is only in extreme cases that the melt should be extra hot. Sometimes we have had extra thin castings weighing several tons that have necessitated exceedingly hot metal.

When the temperature is right, the tests will be approximately the same, no matter how far apart. We have had tests on 30 foot shafts test the same when

they have each been on the extreme ends. When the metal was too hot for the shafts, the test near the pouring gate was lower in tensile strength than the middle test by 3 to 5 thousand pounds, due to oxidation.

In handling composition different obstacles are met with. It is more of a case of molding practice than of alloying, although good melting is necessary. With the best of care in melting, two tests side by side vary considerably, while chemical analysis shows the mixture O. K. The difference in test is due no doubt to cooling conditions, a difference in the temper of the sand, etc. In the following results of tests of two 9-inch angle bypass valves quite a difference is noted. The molds were made the same, as nearly as one man could make them, and the metal given careful attention:

	Tensile strength. lbs.	Elastic limit. lbs.	Elongation in 2 in. %	Reduction in area. %
No. 1 dry sand.....	32,320	18,650	16	1.04
No. 2, green sand....	43,470	16,300	33½	.96
No. 3, dry sand.....	33,720	20,800	15	1.03
No. 4, green sand....	36,500	18,850	16½	1.04

The green sand mold gave the highest tensile strength, but there was a variance in the elongation. The dry sand mold gives more even results, so one would conclude that the dampness of the sand in the green sand mold had an effect on the tests, probably one test was cooled much quicker than the other. The elongation of No. 2 is unusual, the only way I can account for it is that ideal conditions in heat and metal and temper of sand, etc., must have been reached at this point. A chemical analysis showed the mixture to be right with no segregation of tin. These tests are a point for discussion. I should like to hear the ideas of others if they have ever had such a variance. The addition of a small amount of nickel, ¼ of one per cent, to ½ of one per cent materially increases the strength, etc., of 88-10-2. Tests that have gone only 28-33,000 tensile strength on the same molds have gone 38 to 42,000 pounds, with the addition of nickel to the metal. The nickel is added with the copper. One of the necessary things to do to get successful tests in this metal is to add the mixture to the copper at the right temperature. If the copper is too hot, good results cannot be had.

We have made condenser tops weighing 3,800 pounds out of 88-10-2 with the addition of nickel, in the air furnace, putting the nickel in when the copper was nearly melted and adding the tin and zinc when the copper was at the proper heat and had a tensile strength of 52,000 pounds per square inch. For large castings to stand high water pressure the molds should be made out of coarse sand, some core compound that will not scale when being dried, the mold wet-blackened and dried. The pouring temperature has a lot to do with the high tests of any metal. I have mentioned the case of manganese bronze; in 88-10-2 mixture or in any composition, the mold should be poured at the proper temperature. If the metal is too hot, gases

are absorbed from the mold and the metal cuts into the mold, and if too cold the tests are cold short. The pouring temperature for a mold is gained only by experience and judgment. By studying a casting and getting the metal at the right temperature to pour, the tensile strength, etc., has been raised considerably over hit or miss pouring.

TEMPERING TOOL STEEL IN AN ELECTRIC FURNACE.*

The bewilderingly rapid change from the use of the old time carbon steel to the present day special steels, is working a revolution in the methods which were formerly in vogue for tempering carbon steels. Temperatures are demanded which cannot be successfully attained in the ordinary forge without danger of altering the composition of the steel. Perhaps the strongest competitor for the position of a successor to the old forge is the modern electric furnace. The best results so far obtained in a furnace requiring fuel, have been brought about in the following manner.

The tool to be tempered is placed in some sort of a receptacle and all the space between it and the walls of the receptacle is filled with finely divided charcoal. Then the receptacle is sealed up so as to be impervious to gas or air and placed in the furnace. The temperature of the furnace is brought to that required to give the tool the desired degree of hardness (about 2,100° F.), and this temperature is maintained until the heat has had a chance to penetrate entirely through and the whole mass is at one temperature. This requires about two hours. Then the receptacle is removed from the furnace and the tool taken out and plunged into an oil bath. The charcoal does not adhere to the steel. By this method, an excellent job is obtained. An even heating of the steel prevents spring, thus giving accuracy to the result. By packing in charcoal and sealing, exposure to air, gas, or fuel is prevented and consequently the chemical composition is not altered.

The nearest approach to the results obtained in the above manner, are obtained with the use of the electric furnace and as it requires no blast or fuel to obtain a high temperature, the danger of altering the chemical composition is obviated. The highest desired temperatures can be obtained and by varying the strength of the electric current any desired degree of heat can be obtained, or maintained constant.

There are two distinct type of electric furnaces. One type is so constructed that it forms an open vessel in which is placed a substance which becomes a liquid at the hardening temperatures. The substance generally used consists of barium chloride and potassium chloride mixed in the proper proportions, this proportion depending upon the metal to be hardened and the temperatures desired. For very high temperatures, only pure barium chloride is used. In some shops for

temperatures below 700° C. (1,292° F.) pure sodium nitrate is used and sometimes a mixture of sodium nitrate with potassium chloride. The author's experience does not cover use of nitrates. In practice, it has been found that one objection to the use of this method is that the tongs used in removing the tools from the bath, decompose and tiny particles of iron collect on cutting edges and when plunged, these particles become so hard that they can be removed only by grinding. Often it is impossible to grind them off without injuring the tool. Aside from this trouble, very good results are obtained in this furnace. The outer walls of the furnace are never hot, so there is no danger from fire and also the cooling bath may be placed close to the furnace, thus reducing to a minimum the time between removing and plunging.

The other type of furnace does not make use of a heating bath, but consists of a box like structure which may be closed so as to exclude the outside air. The heat is generated by the resistance of carbon "resistors" located in the side walls of the furnace. The current strength and thus the temperature of the furnace is varied by altering the area of these "resistors." The greater the current which is allowed to flow, the higher is the temper obtained. It is generally found that if the furnace is entirely closed, a reducing action takes place, so a door is provided for the admission of outside air until the action is neutral. Care must be taken in using this furnace, that too much air is not allowed to enter, for then oxidation takes place and the steel to be tempered will scale.

The electric furnace has this further distinctive advantage over any kind of a furnace making use of a blast. With such a furnace it is next to impossible to maintain the temperature consistent in all parts so that the tool to be hardened will become hotter on one side than it is on the other, and thus will be sprung out of its true shape. With the electric furnace no draft is required, so that a purely soaking action takes place and the tool is evenly heated.

Granted that the electric furnace can produce just as good work as can be obtained with the most improved practice in the use of the furnace requiring fuel, we must still consider the following points in the operation of the furnace. The furnace is simplicity itself, so that highly skilled and consequently highly paid labor is not required to operate it. By using a pyrometer and knowing the proper temperature at which a given steel is to be hardened, there is no longer the necessity to depend upon the judgment or experience of any one man, thus cutting down labor cost.

An effort is being made to induce capitalists to develop the beet sugar industry in Chile. It is claimed excellent sugar beets can be grown there. Sugar imports amounted in 1911 to 155,644,346 lbs. of raw sugar, of which Peru supplied about 93 per cent, and 26,797,045 lbs. of granulated, of which Germany supplied about 92 per cent.

*From a report presented by B. Hendrickson, at convention of Railway Tool Foremen's Association, Chicago, July 11.

SAMPLING STEEL FOR ANALYSIS.

The following interesting suggestions as to methods of taking samples of steel for analysis by drilling or milling were given by Mr. James H. Herron, Consulting Metallurgical Engineer, in a recent issue of the *Iron Age*:

Too little thought is usually given to the proper method of taking samples of steels for chemical analyses. Any chips that have been a part of the steel, regardless of where or how taken, size, uniformity or degree of cleanliness, are considered good enough for the chemist. Notwithstanding the carelessness with which a sample may be taken, the chemist is expected to make an accurate analysis. If an analysis is necessary, care in taking the sample is justified. The most satisfactory manner of taking a sample for analysis is by one of the following methods:

Drilling—Drilling is usually the more convenient method to use, and the following instructions should

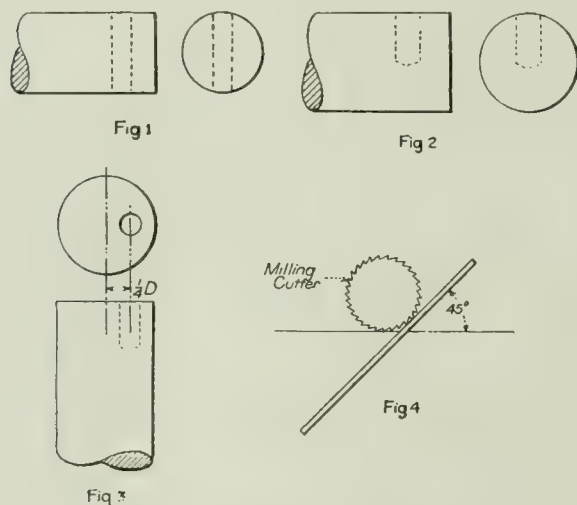


Fig. 1—Drilling Through the Bar
Fig. 2—Drilling to Center of Large Bars
Fig. 3—Drilling Parallel to Axis
Fig. 4—Milling for Sample of Strip

be followed: If possible use a diamond pointed drill. With this the drillings are broken up and of uniform size. If such a drill is not available, the ordinary twist drill may be used. In either case the drilling should be done at a slow speed and with a light feed. Under no circumstances use oil or other cutting compounds. Care should be taken to avoid the use of waste to wipe off any part of the sample from which the drillings are to be taken. Do not drill through the steel into a block of wood. Block the piece up with at least two blocks and drill between them. Care should be taken to avoid handling the sample. It is best to brush off the drillings on a smooth paper or directly into the sampling envelope.

If drilling across a bar, use a drill in size not more than one-half the diameter or side of the bar. For small bars drill entirely through the bar, as in Fig. 1, saving all the drillings. In large bars, drill to the center of the bar, as in Fig. 2. If the bar is too large to drill to the center, discard the first $1/16$ or $1/8$ in. If for a sample a short piece of the bar is available,

it may be drilled parallel to the axis, midway between the center and the circumference, as in Fig. 3. Thin bars or plates should be drilled entirely through, and all the drillings used.

Milling—Any millings are usually satisfactory. The first cut should always be discarded. The instructions regarding oil, cutting compounds or waste, as given above for drilling, should be observed. Where a thin strip or wire is available the sample should be taken at an angle of 45 deg. with the axis of the piece, as in Fig. 4. For a complete analysis the samples should be between 1 and 2 oz.

Failure to observe the above instructions may introduce some foreign element and render the analysis worthless.

During the month of August the United States Geological Survey appraised 1,219,187 acres as coal land in the Western states, placing a valuation thereon of \$19,623,196. In the same month the Survey also classified 126,174 acres as noncoal land and transmitted the findings to the General Land Office so that the land might be restored to the public domain. These classifications were based on the field examinations of the Survey geologists. In connection with the classification of oil land the Secretary of the Interior withdrew in August 36,746 acres in Wyoming, making a total of 4,810,928 acres of oil land now standing withdrawn and awaiting needed legislation in the interests of the development of the nation's extensive petroleum deposits. In administration of the phosphate lands, 8,140 acres in Florida were withdrawn and 45,381 acres in Wyoming were restored to entry, leaving a total of 3,303,320 acres of phosphate land standing withdrawn and also awaiting necessary legislation. The content of the important deposits on these lands has been moderately estimated at over two billion tons of high-grade phosphate rock.

The calico printers of the Manchester district, England, are considering the formation of an organization to be called the Federation of Calico Printers. It is stated that the project has the support not only of the Calico Printers' Association but also of leading firms outside that combination. The federation is to be virtually an inner council of the trade. Of its purposes, the establishment and maintenance of a fixed price list is in the forefront. It is proposed that all disputes as to "allowances" and other matters shall be referred to the executive committee of the federation for its consideration and adjustment. This committee will be representative, and will be chosen on a basis of "machine" proportion. The formation of such a federation would, of course, be likely to have a considerable effect on the future of the calico-printing trade. It is somewhat significant that the movement should be almost simultaneous with the effort of the Australian calico printers to end the competition among themselves, where a reduction of prices to stimulate consumption proved a failure.

A SPECIAL TYPE OF ELECTRIC FURNACE.

In a paper presented at the 19th general meeting of the American Electrochemical Society, Mr. Thaddeus F. Baily described an electric furnace evolved out of experiments commenced over four years ago. Mr. Baily's paper practically in full, was as follows:

The furnace is of the resistance type, and consists essentially of two carbon electrodes, spaced from each other, and an intermediate resistance body of a carbonaceous composition in which the heat is generated. In the space directly above the resistance material and directly under the roof of the furnace is placed the metal to be heated, a ledge at the rear of the furnace and one at the opening supporting the material to be heated. Reference may be made to Fig. 1, a right-left section; to Fig. 2, a front-back middle section; and to Fig. 3, a sectional plan of the furnace.

The electrodes enter the furnace through the rear wall, and are placed slightly convergent, so that the

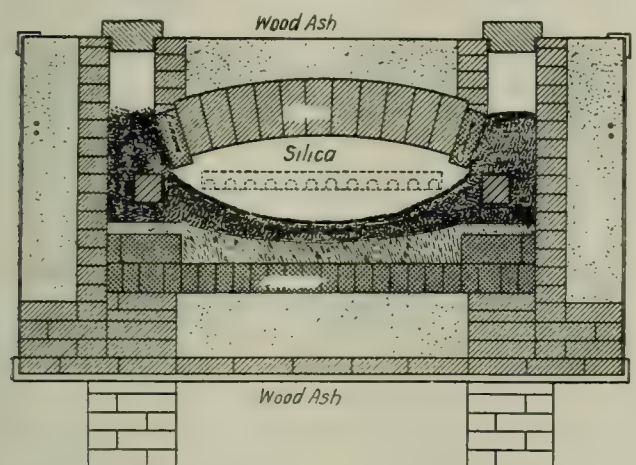


Fig. 1—Vertical Right Hand Section of Electric Furnace of Resistance Type.

path of the electric current will be shorter from electrode to electrode at the front of the furnace than at the back. This arrangement compensates for the cooling effect, which is greater in the front of the furnace on account of the opening and the charging of the cold material.

The electrodes entering the furnace from the rear present comparatively large contact surfaces to the resistance material, without the use of special electrode sections. The electrodes are also placed in a plane above the resistance material, which throws the shortest path for the electric current in the upper part of the resistance body and nearest the metal.

This is a feature that seems almost indispensable to the successful operation of a furnace of this character, since in the furnaces constructed without this feature the cooling of the upper part of the resistance body by the cold steel caused the electric current to take a lower path, in which portion of the body the temperature became very high and melted out the bottom linings and the bottom of the furnace itself, and at the

same time did not maintain the heating chamber at a temperature high enough to heat the metal.

The resistance material is composed of coke or coal. Crushed foundry coke passing over a 0.25-in. (6 mm.) ring and through a 0.37-in. (9 mm.) ring giving the most satisfactory and uniform results. For a 40-kw.

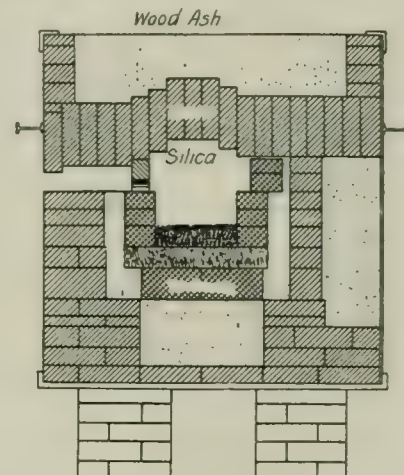


Fig. 2—Section Front to Back Through Middle of Furnace.

furnace, heating 150 lbs. (69 kg.) of metal per hour, the distance between electrodes should be 36 ins. (90 cm.) and the cross-sectional area about 24 sq. ins. (150 sq. cm.). To maintain an electrical input of 40 kw., a voltage of 200 would be required with a coke resistance body; if the body is composed of coal, the voltage should be about 150 volts.

It is extremely difficult to determine the effective cross-sectional area of the material through which the electric current passes, as at working temperatures the lining materials become almost as good conductors of electricity as the resistance material itself. The resistance body as it approaches the electrodes has a very

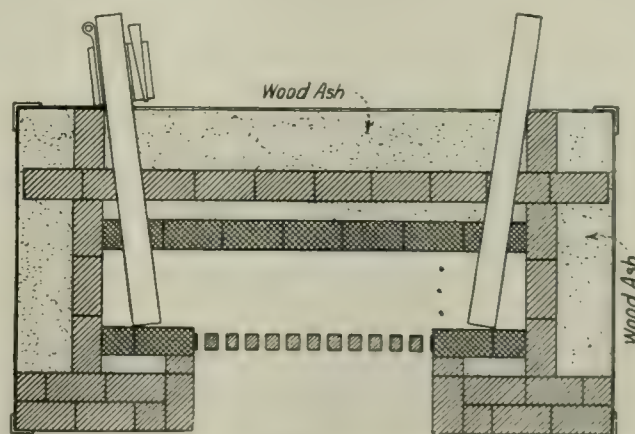


Fig. 3—Horizontal Section Through Furnace.

greatly increased cross-section, so as to provide a better contact with the electrodes, prevent undue heating at the point of contact, and prevent, to as great an extent as possible, the dissipation of heat through resistance to the passage of the current except at that part of the resistance body directly under the metal.

Thus in a way these increased cross-sections per-

form the mission of electrodes, as they conduct the current from the electrodes proper, which are located in a protected part of the furnace, to the part where the transformation into heat is desired, and they do this without any considerable heat being generated in these portions themselves.

The most serviceable lining material so far obtained is made of chrome brick and chrome ore, and while a certain reducing action takes place between the chrome ore and brick and the carbon of the resistance material, it is not of such nature as to seriously impair its usefulness as a lining material. This chrome lining is carried up to at least one course above the resistance material. The lining is readily accessible for repairs or inspection by removing the three courses of silica brick directly under the furnace opening.

The top of the furnace is composed of silica arch brick, and is 9 ins. thick, and clamped from front to back. A row of chrome arch brick is placed at each side of the roof to prevent contact of the silica brick with the carbon in the hoppers above the electrodes.

The sides of the furnace are composed of silica brick and, in the larger furnaces, are incased in a sheet steel frame. Insulating material is placed between the silica brick and the casing.

The furnace base consists of a heavy cast-iron plate supported by cast-iron legs or brick piers.

The cable terminals are connected with the electrodes by means of iron sleeves, copper straps and iron wedges. In making the connection, the iron sleeve is placed over the end of the electrode and copper straps placed against the four sides of the electrode. The copper cable terminal is then placed between one of the copper strips and the iron sleeve, and wedges driven in on the opposite side between the strap and sleeve, and a firm contact thus secured. Wedges are then driven in on the other two sides between the copper strips and the sleeve. In this way the current flow is equally distributed on all four sides of the electrode by means of the encircling iron sleeve.

The furnace is controlled by means of a regulating transformer and controller. The transformer gives full rated output at the lowest voltage rating. While hand regulation is usually provided, the regulation may be made automatic at a slight additional cost. A voltage range of from 33 to 50 per cent is usually provided, depending on the operating and starting requirements.

Each furnace is provided with a single-panel switchboard having mounted on it a voltmeter, ammeter, watt-hour meter, circuit-breaker and oil switch. The voltmeter and ammeter indicate at all times the conditions in the interior of the furnace, as irregularities are readily noticeable on the instruments. The watt-hour meter enables accurate data to be kept on the current consumption for heating any particular class of work.

The temperatures that may be obtained are limited solely by the electrical input and the temperatures al-

lowable by the refractory linings of the furnace. The temperature usually maintained in a furnace for the rapid heating of stock is such as to cause the fusion of the ends of the silica brick forming the roof and is probably not less than 3,200° F. (1,765° C.). The resistance material, of course, reaches a much higher temperature. When working at the highest temperatures usually met in forge practice, a renewal of the lining of the bottom of the furnace will be required every two to three weeks.

The replacing of the lining or portions of it and the replenishing of the resistance material are the only items that may be classed as renewals, and should not exceed, in furnaces heating 150 lbs. of metal per hour, working at the highest temperatures, an average of 20 cts. per day for lining material and 5 cts. per day for resistance material.

The metal being heated is maintained in a reducing atmosphere, the high temperature carbon resistance material giving off a gas of a reducing nature. The electric furnace is the only furnace built in small units in which both a high temperature and a reducing atmosphere may be maintained. The saving in oxidation loss is very considerable in small furnaces of this character, as the loss from oxidation in the usual combustion furnace is the cause of the loss of a large number of forgings, due to the fact that a piece of stock, having lost a considerable amount of metal by the oxidizing flame of the combustion furnace, does not contain enough metal to fill the dies.

The thermal efficiency of the furnaces varies with the size, the percentage of operation at full capacity and the ruling temperature required. Efficiencies of from 33 to 65 per cent may be expected in furnaces with heating capacities of from 120 lbs. (55 kg.) per hour to 1,000 lbs. (455 kg.) per hour.

An experimental furnace was installed at the plant of the Transue & Williams Co., and a description of the apparatus and results obtained may be of interest.

The power for driving the generator was supplied by a 12 by 16-in. (30 by 40 cm.) Buckeye four-cylinder twin single-acting gas engine, which not only drove the generator for supplying current to the furnace, but also for driving a portion of the motors in the machine shop, so that only part of the time was sufficient power available for furnace operation.

Belted to the flywheel of the gas engine was the 120-kw., 2-phase, 440-volt revolving field alternator, only one phase of which was connected up. The leads from this phase were connected with the low-tension terminals of a 37.5-kw., 440 to 2,200-volt transformer. The current was then stepped down by means of a 2,200-220 or 110-volt transformer, the coils on the low-tension side being so connected through a double-throw switch for either series or parallel operation, so that a normal voltage of either 110 or 220 volts could be obtained. The variations between 110 volts and 220 volts on the lower voltage and also on the voltages

above 220 were obtained by varying the field of the alternator.

By this arrangement a possible voltage range could be obtained of from 90 to 300 volts, which was more than ample for conditions of operation. Inability to readily obtain a 2,200-volt generator of proper size accounted for the use of the 440-2,200 step-up transformer. From the double throw switch the current was conducted to the furnace located in the forge shop, some 75 ft. (22 m.) distant.

The instruments mounted on the switchboard consisted of a 150-volt voltmeter and a 600-ampere ammeter, both made by the Westinghouse Electric & Mfg. Co. The voltmeter was so connected that when the low-tension coils of the step-down transformer were thrown in parallel, the instrument gave a direct reading, and when in series, the indicated voltage was half the actual voltage.

The furnace was constructed substantially in accordance with the description given in the first part of this paper, except that air spaces were used in place of the insulating material shown in Fig. 2, and it was rated as a 40-kw. unit, having a heating capacity of 120 lbs. (55 kg.) per hour, the heating capacity being rated somewhat lower than the usual practice on account of the high temperature required.

The electrodes were 4 by 4 by 48 ins. (10 by 10 by 120 cm.) long, composed of carbon, and were spaced 36 ins. (90 cm.) from each other. The cross-sectional area of the resistance material was approximately 24 sq. ins. (150 sq. cm.). The walls were composed of 9 ins. (22.5 cm.) of silica brick, and were of rather loose construction, owing to the numerous changes that were made and to the jar from the hammers in the plant.

A voltage of 250 volts was usually used in starting the furnace in the morning. From one to two hours was usually required to bring the furnace up to temperature. The voltage was then reduced to about 200 volts when using a coke resistance body, or 150 volts for a coal body, which tensions enabled the required electric input to be maintained.

Some of the various linings used before the chrome lining was selected were magnesia, carborundum and silica. The chrome lining, however, gave by far the most satisfactory and uniform service, lasting three weeks without renewal or repair. As only the bottom lining is subjected to very high temperature, it is practically the only part requiring renewal, and as the usual bridge wall is not required, that saving compensates for the cost of renewals of the lining of the electric furnace.

The Hungary Steel & Iron Works at Hankow, China, in 1910 produced 130,000 tons of iron, of which 14,034 tons was sent to Shanghai and other Chinese ports, while 29,000 tons was shipped to Japan and 150,000 tons to America. The output of iron ore in 1910 from the Tayeh mines amounted to 303,000 tons.

A NEW VOLUMETRIC METHOD FOR TIN.

Numerous methods for the determination of tin have been tried out in the laboratory of the McCormick Works of the International Harvester Co., with various degrees of success. Gravimetric methods giving results of the required accuracy are too lengthy and tedious for ordinary use in laboratories where it is required to complete a large number of determinations in a short time. Shorter schemes, such as weighing the combined oxides of antimony and tin, determining antimony in a separate sample, and calculating tin by difference, cannot be used for alloys containing lead, copper, or numerous other metals which are to be found in some commercial alloys, unless the amount of these impurities contaminating the oxides be determined and taken into consideration.

The volumetric methods proved to be rather unsatisfactory, especially if the titrating solution was standardized against a standard reducing solution in preference to C. P. tin. It was found that determinations on quantities as small as 5 per cent were unreliable, and that on high percentages it was almost impossible to obtain consistently accurate results even if the oxidizing solution was standardized against an equivalent amount of metal treated in an exactly similar manner.

Endeavoring to overcome these difficulties, the method to be described was finally adopted. A description of this method is given by Messrs. Wilbur W. Patrick and G. C. Wilsnach in the Journal of Industrial and Engineering Chemistry, from which the matter in this article has been taken. The results obtained are consistent and correct to within 0.2 per cent on amounts of 50 per cent or over and considerably more accurate on smaller percentages. As large percentages of copper, lead, nickel, and perhaps other metals not experimented with, interfere, it has been found expedient to modify the method somewhat in the presence of these elements. Both determinations will be described.

REGULAR METHOD.

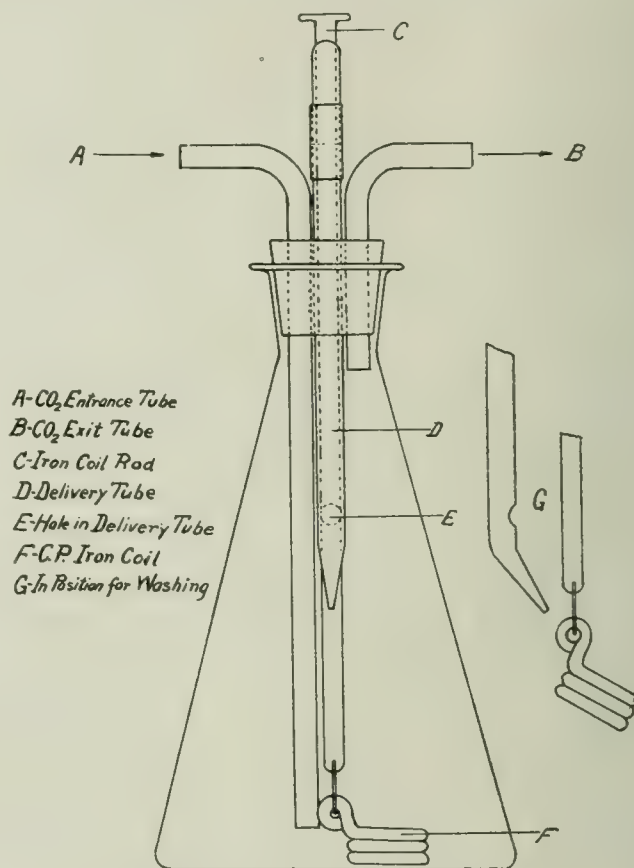
The following scheme of analysis is available where no more than 5 per cent of either lead or copper is present in the alloy. Where the percentages of these elements exceed this limit a modification of the method is necessary.

Place an amount of sample corresponding to 0.5 gram or less of tin in a 500 cc. Jena Erlenmeyer flask and add 0.15 gram C. P. metallic antimony if as much or more is not already present in the alloy. If the sample contains less than this amount it is necessary to make up the deficiency. Add 10 cc. of concentrated sulphuric acid and heat to effect solution. Remove from the hot plate and cool. Dilute the cold sulphuric acid solution with 10 cc. of water, add 60 cc. of concentrated hydrochloric acid, and then 40 cc. more of water. Prepare a four-hole rubber stopper that fits the neck of the flask. Through one hole pass a glass tube bent at right angles

reaching to the bottom of the flask and through the hole diagonally opposite insert another tube bent in a similar manner but extending only a short distance below the bottom of the stopper. Through the third hole pass a long thin glass rod fitted with a 2-in. piece of platinum wire. This rod should fit rather snugly without, however, giving any difficulty to the operator in raising or lowering it during the determination. The platinum wire is now bent into the shape of a hook and a piece of very nearly C. P. iron wire attached. Swedish iron in plates of $\frac{1}{8}$ -in. thickness cut into strips of $\frac{1}{8}$ in. in width and $3\frac{1}{4}$ ins. in length, curled up in the form of a spiral, will suit the purpose well. Through the fourth hole pass a $\frac{1}{2}$ -in. tube 4 ins. long and drawn out at the lower end to an opening small enough to enable the operator to introduce iodine solution in sufficiently small quantities to obtain the starch iodide reaction within one drop of titrating solution. The trapped end is bent slightly in the direction of the submerged wire for the purpose of conducting a stream of water to free the iron from adhering tin solution after it has been withdrawn from the liquid. This delivery tube should also be provided with a $\frac{1}{4}$ -in. hole about $\frac{3}{4}$ in. above the lower opening to afford a means of escape for the carbon dioxide gas which is being rapidly introduced during the titration. A carbon dioxide generator is connected to the long tube while a piece of rubber tubing connects the short tube opposite to a 100 cc. pipette which dips into a reservoir of water. This automatically prevents any air from entering the system when a partial vacuum is formed in the flask during the determination, which cannot be taken care of by the entering carbon dioxide gas. Having attached the iron to the platinum wire, the rubber stopper is firmly placed in position in the neck of the flask and the rod lowered so that the spiral of wire rests on the bottom of the flask. The generator and water seal are attached as previously described, a cap is placed over the opening of the large delivery tube and a rapid stream of carbon dioxide gas passed through the system. After a few minutes it may safely be assumed that all of the air is expelled from the flask, whereupon heat is applied and the contents permitted to boil for 25 minutes. The solution when first placed in the flask appears a deep yellow or orange, depending, of course, upon the constituents present, but shortly before commencing to boil it becomes colorless and finally black, due to the liberated metallic antimony. After the reduction is complete, remove the burner, plunge the flask into a large container of cold water and allow to remain until thoroughly cold. The iron wire is then raised to a position directly below the end of the delivery tube. The cap of this tube is then removed and with all possible haste a stream of cold *freshly boiled* water permitted to play upon the spiral to free it from any adhering tin solution, after which the wire is raised so that the titrating solution will not come in contact with it. Freshly prepared starch is added and, without in-

terrupting the passage of gas, standard iodine solution introduced into the flask as fast as the burette will permit. When near the end point, which is indicated by the reluctant disappearance of the blue, the titration can be carried on very slowly until completed. The blue of the starch iodide is not permanent, disappearing after a minute or two, which fact does not, however, detract from the accuracy of the determination.

It is not to be understood that the tin is completely reduced by the direct action of the iron alone, neither will the addition of pulverized metallic antimony bring about the desired result. However, this metal as deposited is in a state where its chemical activity is at a



Arrangement of Volumetric Tin Apparatus.

maximum, thus enabling it to fully complete the reduction.

Standardize the sodium thiosulphate, which serves to determine the strength of the iodine solution, very carefully against a bichromate or permanganate solution of known strength. It is essential that the utmost accuracy be employed in the above standardization, since 0.1 cc. more or less of a N/10 oxidizing solution makes a considerable difference in the ultimate tin value of the iodine. It has been found advisable in finding the normality of a freshly prepared iodine solution to check the theoretical standardization against C. P. tin.

MODIFIED METHOD.

A modified method is used when 5 per cent or more of copper or lead, or any other interfering element, is present in the specimen to be analyzed.

Place 0.5 to 1 gram of sample in a small casserole and add if necessary 0.15 gram of antimony as in the regular method. Cover the sample with 8-10 cc. of concentrated nitric acid and evaporate to dryness. It is advisable in order to facilitate the subsequent filtration to bake strongly for about 15 minutes. Cool and add 20 cc. of 1-1 nitric acid, and, after breaking up the lumps with a stirring rod, filter and wash several times with hot water. If the baking has been conducted properly no traces of oxides will be discernible in the filtrate. The precipitate with the filter paper is then placed in a 500 cc. Jena Erlenmeyer flask and treated with 20 cc. of concentrated sulphuric acid and 2 grams of potassium sulphate. Place the flask on a piece of asbestos over a medium hot burner and heat carefully till the first violent reaction is over, after which the heat can be increased. Towards the end of the oxidizing operation, while the liquid is still black however from the free carbon present, the flask and contents should be cooled and the sides of the con-

duced offsetting in a large measure the water used for washing. Antimony present up to 25 per cent will not obscure the end point, provided a good light and white background are available.

Table I gives a few results obtained on mixtures containing various amounts of copper, lead and nickel as noted. These figures are fairly representative of the results which may be obtained by the methods described in the preceding pages.

TABLE I.

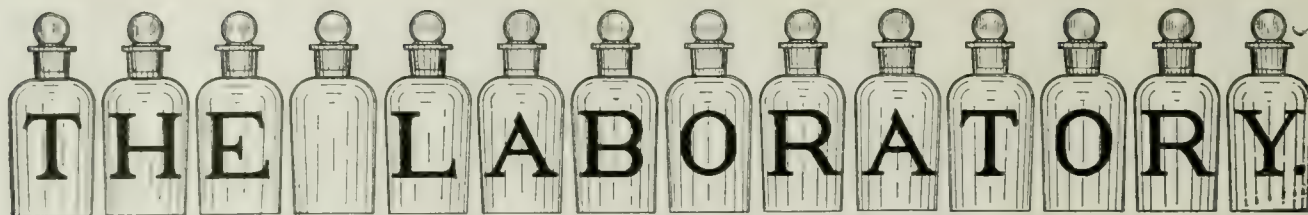
Method.	Approximate amount.			Tin taken. Gram.	Tin found. Gram.	Error. Mg.
	Copper. Gram.	Lead. Gram.	Nickel. Gram.			
Regular				0.4040	0.4038	0.2
Regular				0.0568	0.0575	0.7
Regular	0.03			0.4470	0.4478	0.8
Regular	0.05	0.05		0.1143	0.1153	1.0
Modified	0.25	0.30		0.4060	0.4065	0.5
Modified	0.03	0.66	0.03	0.1764	0.1763	0.1
Modified		0.30	0.05	0.4272	0.4261	1.1
Modified	0.15	0.80		0.0216	0.0214	0.2
Modified	0.08	0.80		0.1000	0.1000	0.0
Modified	0.50			0.4530	0.4526	0.4

tainer washed down with a stream of water. The particles adhering so firmly to the wall of the flask that the water does not loosen them should be brought back into the main solution with the aid of a "policeman." The removal of the carbon should by no means be hastened by the addition of an oxidizing agent, since this will cause the antimony to assume the pentavalent form, which must be avoided. The addition of the water will now have a tendency to again cause frothing when the heat is applied, making it necessary to conduct this operation very carefully. From 2-2½ hours are usually required, depending upon the intensity of heat employed, to rid the solution completely of the carbon. Cool, introduce the required amount of water, but add only 45 cc. of hydrochloric acid instead of 60 cc. as in the regular method.

If very large percentages of antimony are present, enough to obscure the end point obtained with the starch solution, it is well to treat in the usual manner up to the point where the metallic antimony separates out. The solution should then be rapidly cooled, filtered with suction and washed with hot water. About 0.10 gram of metallic antimony, which has previously been dissolved in a few cc. of sulphuric acid, is then added, the solution returned to the original container, and the reduction continued. The concentration of the solution after this operation should not be changed to any great extent, the additional acid intro-

The iron ore marketed in the United States in 1911, according to figures of the Geological Survey, amounted to 40,989,808 long tons, valued at \$86,419,830 at the mines, compared with 56,889,734 long tons, valued at \$140,735,607, in 1910. Minnesota and Michigan produced the bulk of the iron ore, the former 23,398,406 long tons and the latter 8,944,393 long tons. During the year 159 mines produced over 50,000 long tons of iron ore each, compared with 191 mines which exceeded that output in 1910. The largest quantity produced by any single mine in 1911 was 1,553,510 long tons, from a mine at Marble, Minn. The production of pig iron in 1911 amounted to 23,257,288 long tons, valued f. o. b. at the furnaces at \$327,234,624, compared with 26,674,123 long tons, valued at \$412,162,486, in 1910, a decrease in quantity of 3,416,835 tons and in value of \$84,827,862. Pennsylvania produced the greatest quantity of pig iron, 9,581,109 long tons; Ohio was second, with 5,371,378 long tons, and Illinois stood third, with 2,036,081 long tons. The total quantity of steel produced in 1911 was 23,675,501 long tons, against 26,094,919 long tons in 1910. The bulk of it came from Pennsylvania, whose output was 13,207,539 long tons.

The U. S. Consul at Leeds, England, gives the following description of the work of rawhide pickers at the plant of Thomas & John Walton, picker makers, Stonewood Mills, Todmorden. The hides are soaked in lime pits and then dehaired. Piecework is the method, and a man can handle 900 hides per week and makes 35s (\$8.52). A deliming process also takes place to fit some requirements, the picker being then more ready to take the seasoning of fish oil, which, properly incorporated, makes for the life of the picker. Shapes are cut by machine and are molded by hand on dies, which are then machined to finish. One noted a certain process of the finishing (the trimming of extended edges of inner layers of the bend of the picker after pressure in the machine), being by hand and by means of the homely pocketknife—room here possibly for some handy contrivance. Present price of finished pickers is about 33 cents per pound. It was interesting to learn that wastes are exported largely to the United States, where, it is stated, they go into the manufacture of sizes, etc., and probably find an ultimate use in the preparation of paper for banknotes. Todmorden is the home of the picker industry, and of the 32 picker mills in Europe 18 are located at Todmorden.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR IN- STITUTE OF TECHNOLOGY.

The Analysis of Iron and Steel.

In the analysis of ordinary iron and steel, the following determinations are made: Silicon, sulphur phosphorus, manganese, and carbon.

Those iron alloys containing nickel, chromium, high percentages of manganese, tungsten, molybdenum, vanadium, etc., commonly known as "special" or "high speed" or "self-hardening" steels require for their analysis special methods, not only for the determination of their extraordinary constituents, but also in many cases, for these substances common to all steels, such as phosphorus and silicon.

Two methods are described for each determination; one a method designed to give results of an accuracy sufficient for all ordinary purposes in the shortest possible time and the other, to give the most accurate results without special regard to time.

THE DETERMINATION OF SILICON.

The chemistry of the determination of silicon is the same for all methods. It consists in oxidizing the Si present in the metal to SiO_2 and silicic acid (H_2SiO_3), dehydrating the latter, and separating the SiO_2 along with some carbon, by filtration, burning off the carbon, correcting for the iron oxide in the residue of silica, and calculation from the weight of SiO_2 . The differences are in the means employed in accomplishing these results.

Drown's Method: 1 gram of sample is weighed out into a four-inch casserole and treated with 15 to 20 cc. of 1:1 nitric acid. The solution is boiled until there is no further action when 10 cc. of concentrated sulphuric acid is added and the whole evaporated over the free flame to copious fumes of sulphuric acid. This accomplishes the oxidation of the silicon and also the dehydration of the silicic acid. After cooling the mass is taken up in water (100 cc.) and the mixture boiled for several minutes to assure the complete solution of the ferric sulphate. It is then filtered, and the residue washed first with dilute hot (1:2) HCl and then with hot water. The residue consisting of SiO_2 and carbon is burned without previous drying in a platinum crucible, ignited over the blast lamp for five minutes, cooled and weighed. Since it always contains traces of iron oxide it is necessary to make a correction, as follows: To the residue in the crucible one drop of H_2SO_4 is added and 2-3 cc. of HF, and the mixture evaporated dry on the hot plate. This

treatment expells the SiO_2 as SiF_4 . Crucible and residue are ignited gently with a moving flame until all acid is driven off, when the ignition is finished over the blast. The weight of crucible and residue of Fe_2O_3 subtracted from the previous weighing gives the corrected weight of SiO_2 .

$$\frac{\text{Wt. SiO}_2 \times 0.4693}{\text{Wt. of sample}} = \% \text{ Si}$$

Wt. of sample

This method yields results satisfactory for most purposes and is quite rapid on account of the speed with which the sulphuric acid dehydrates the silicic acid as compared to other means of dehydration.

A slightly more accurate method follows:

The 2 gm. sample is treated with 25 cc. of nitric acid (1:1) in a beaker, the beaker covered and the whole heated on the hot plate until the iron is dissolved and no more nitrous fumes are given off. The solution is then transferred to a small casserole, evaporated to dryness on the hot plate and ignited, with constant stirring, over the free flame until all ferric nitrate is converted into oxide. After cooling, the residue is covered with 30 cc. of concentrated HCl and heated almost to boiling, the ferric oxide and every thing other than silica and some graphite going into solution. The whole is then evaporated to dryness over the water bath and the residue baked for an hour at 120 degrees. After cooling the residue is moistened with about 5 cc. of concentrated HCl, allowed to stand a few moments, taken up in boiling water and filtered. After washing first with dilute HCl and then with hot water the residue is ignited, and the weight of silica corrected for traces of iron just as described in the method given above.

THE DETERMINATION OF SULPHUR.

A volumetric and a gravimetric method are described. Of these the volumetric, usually called the evolution method, is by far the more rapid, but it gives results that are consistently a little lower than those obtained by the gravimetric process. In reporting the determination of sulphur it is therefore the custom to state which method has been used.

Sulphur by Evolution: This method depends upon the following chemistry: Sulphur is present in the form of sulphides of iron and manganese. The sample is treated with HCl and the evolved gases, hydrogen, hydrocarbons, phosphene and hydrogen sulphide, passed through a solution of sodium hydroxide. The NaOH absorbs the H_2S forming Na_2S . This solution, in rather large bulk, is then acidified, with the liberation of H_2S , which remains in solution, and

the H_2S is titrated by standard iodine solution according to the reaction:



The iodine solution is prepared by dissolving 1 gm. of iodine with 3 gm. of KI in 50 cc. of water and diluting the solution to one liter. This is best standardized by titrating the H_2S liberated from a sample of standard steel of known sulphur content treated in exactly the same manner that the samples for analysis are treated. Such samples of standard steels, which may be used in the standardization of solutions for the determination of phosphorus and manganese as well as for sulphur, may be obtained from the U. S. Bureau of Standards.

Before applying the evolution method to hardened steel or white iron, the samples should be annealed

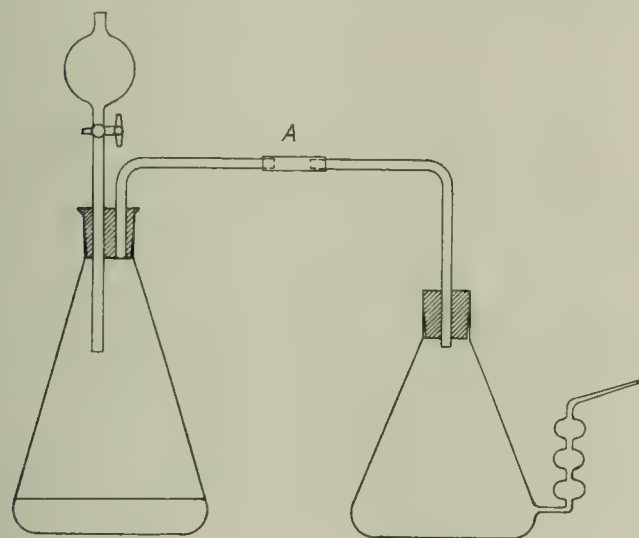


Fig. 1.

by heating to a temperature of 500°C . and allowing to cool slowly.

Five (5) gm. samples of steel (or two (2) of pig iron) are placed in evolution flasks and the delivery tubes connected with a Fresenius absorption tube as shown in Fig. 1. The absorption tube contains about 50 cc. of NaOH , sp. gr. 1.2. The sample is covered with 20 cc. of water and an equal volume of concentrated HCl added through the dropping funnel. Heat is applied gently until all evolution of gas ceases, and the solution is then boiled for twenty minutes more. The connection is then broken at A and the solution rinsed into a 400 cc. beaker where it is made strongly acid with HCl . The total volume should exceed 250 cc. Starch solution is now added (2 cc.) and the H_2S titrated by iodine solution.

In the standardization:
$$\frac{\% \text{ S.} \times \text{wt. sample}}{\text{cc. I sol.}} = \text{wt. S}$$
 per cc. of I sol.

In the determination:
$$\frac{\text{S per cc.} \times \text{vol. of sol. used}}{\text{wt. of sample}} \times 100 = \% \text{ S.}$$

The iodine solution not being perfectly stable, its standard should be frequently checked.

The Oxidation Method.—It is of the highest importance that all operations in the gravimetric method for sulphur be carried on in an atmosphere free from the vapors of sulphuric acid.

The chemistry of the method is simple. It consists in oxidizing the sulphur present in the metal by strong nitric acid, removing the silica and graphite by filtration and precipitating the sulphuric acid with barium chloride as BaSO_4 , in solution free from nitric acid, but containing enough hydrochloric to hold all iron and phosphoric acid in solution.

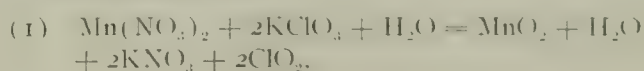
The sample of from 2 to 5 grams is treated with 20 to 40 cc. of HNO_3 and warmed carefully until the rather violent action ceases, when the solution is evaporated to dryness on the hot plate. The residue which should not be baked, is taken up in hydrochloric acid (10 cc.) and again evaporated dry. Complete elimination of nitric acid and dehydration of silica is accomplished by again taking up the residue in hydrochloric acid and water, evaporating to dryness on the water bath and baking for a half hour at 120°C . The residue is moistened with 10 cc. of hydrochloric acid, 50 cc. of hot water added, and the whole boiled a few moments, filtered and the residue washed. To the boiling hot filtrate ten cc. of a 10 per cent solution of BaCl_2 is added and the whole boiled for fifteen minutes, when it is set aside to stand over night. The clear filtrate is decanted through the paper, the main bulk of the filtrate removed and replaced by a small clean beaker and the precipitate rinsed onto the paper where it is washed free from iron by hot water. If any of the precipitate goes through the paper, the filtrate should be refiltered through the same paper until perfectly clear. The paper is burned in a platinum crucible and the precipitate ignited for several minutes until white at the full heat of the Bunsen burner, when it is weighed and sulphur calculated.

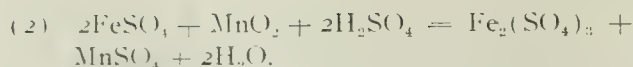
$$\frac{\text{weight BaSO}_4 \times 0.1374}{\text{weight sample}} \times 100 = \% \text{ S.}$$

THE DETERMINATION OF MANGANESE. (Williams).

The chemical principles employed in this excellent method are the following: Hydrated MnO_2 is precipitated quantitatively from solutions of manganous salt in the presence of concentrated nitric acid by potassium chlorate. All hydrochloric acid must be absent. The precipitate is soluble in an acid solution of ferrous sulphate, and when a known volume of standard solution is employed, and the excess of ferrous iron titrated by standard permanganate, the weight of manganese may be calculated.

The reactions are:





Since $2\text{KMnO}_4 = 10\text{Fe}$ and $2\text{Fe} = 1\text{Mn}$, then
 $2\text{KMnO}_4 = 10\text{Fe} = 5\text{Mn}$.

and the Mn standard of a permanganate solution is calculated from the following proportion:

$10\text{Fe} : 5\text{Mn} :: \text{Fe standard} : \times (\text{the Mn standard}).$

Procedure: The 2.5 gm. sample of iron or steel is placed in a 500 cc. Erlenmeyer flask and to it is added 50 cc. of nitric acid (1 HNO_3 : 1 water). After complete solution the solution is evaporated to about 15 cc., cooled, and 50 cc. HNO_3 (sp. gr. 1.42) and 3 gms. of potassium chlorate crystals added, the whole being boiled for fifteen minutes. The solution is then cooled, and the treatment with concentrated nitric acid and potassium chlorate repeated. After again boiling for a few minutes, the precipitate of hydrated MnO_2 is filtered through asbestos on a Gooch crucible, washed free from iron with concentrated nitric acid and finally free from acid with hot water. The asbestos felt with the precipitate is removed from the crucible and returned to the original flask where 50 cc. of a standard solution of ferrous sulphate is added to it. After thorough shaking to assure complete solution of the precipitate, the excess of ferrous salt is titrated with standard potassium permanganate solution. The volume of permanganate used by the manganese is equal to the volume required for the 50 cc. of ferrous solution minus the volume of permanganate used for the excess of ferrous solution.

$$\frac{\text{Mn std. of KMnO}_4 \times \text{vol. used}}{\text{weight of sample}} \times 100 = \% \text{ Mn}.$$

The permanganate solution is the ordinary solution used for the titration of iron; about tenth normal in strength. The ferrous sulphate solution is usually made about twice as strong, i. e., fifth normal, or about 80 grams of ferrous ammonium sulphate per liter. It is prepared by mixing 900 cc. of water and 100 cc. of concentrated sulphuric acid and dissolving in it 80 grams of ferrous ammonium sulphate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$). This solution is more stable than the solution of the single ferrous sulphate, but its ratio to the permanganate solution should be re-determined frequently.

THE COLORIMETRIC METHOD FOR MANGANESE.

This method is in quite general use, but it demands very careful manipulation and strict adherence to conditions for its successful application. It is never so sure as the standard volumetric methods, but it is very rapid and under the proper conditions may be made sufficiently accurate for ordinary routine work. In principle the method is as follows: The sample of steel is dissolved in nitric acid, along with an equal weight of a sample of steel of known manganese content, and the manganese is oxidized to permanganic acid by means of a persulphate in the presence of silver nitrate. The solutions are made up to definite volumes,

and the colors of equal volumes of the two solutions matched by dilution in colorimeter tubes. When the colors match exactly, the percentage of manganese in the unknown sample is to the percentage in the standard sample as the volumes of the two solutions in the tubes, i. e., $x(\text{unknown } \% \text{ Mn}) : \% \text{ Mn in standard} :: \text{vol. of unknown} : \text{vol. of standard}$.

Procedure in Steels.—The 0.1 to 0.2 gram samples of steel (unknown and standard) are treated in large test tubes, with 10 cc. nitric acid, sp. gr. 1.2, and heated in a vessel of boiling water until solution is complete, when they are boiled gently over the flame until nitrous fumes are expelled. 15 cc. of silver nitrate solution (1.33 grms. per l.) are added, immediately followed by about one gram of ammonium persulphate. Heat until the color of permanganic acid begins to develop and about one-half a minute longer, and then place in cold water—during the evolution of oxygen. Dilute the solutions of sample and standard to 100 cc. in volumetric flasks and compare equal volumes (10 cc.) in comparison tubes.

If the color, as it develops, shows the slightest tinge of brown, the determination is worthless and should be repeated.

According to the Manchester (England) Guardian, there have been marked developments in the productive capacity of the artificial silk industry during the past year, particularly in Russia, where the ordinary silk trade is also making good progress. A new company has just been formed with \$600,000 capital to erect a plant near Moscow. The style of the undertaking is the "Soie Artificielle de Mysbow." A fairly large works has been producing in Moscow for some time past, and it is stated that arrangements are being made for increasing the output. The company which began manufacturing in Tomaschow at the commencement of the current year has been very successful, and further undertakings will shortly be put forward in Russian Poland.

During the last few years the United States Geological Survey has received so many inquiries with regard to methods of prospecting for iron ore, that suggestions regarding prospecting for certain types of ore, such as hematite and limonite, have been published in an advance chapter on iron ore from "Mineral Resources of the United States for 1911," by Ernest F. Burchard, a copy of which may be obtained free on application to the Director of the United States Geological Survey at Washington, D. C. Prospecting by pits, drills and magnetic surveys is discussed, but owing to the variety of ores and to the differences in local conditions of climate, topography, geologic associations, and structure, the suggestions given are very general. It is hoped, however, that a few of the fundamental principles at least may be made clear.

THE IGNITION OF PRECIPITATES WITHOUT THE USE OF THE BLAST LAMP.*

By PERCY H. WALKER and J. B. WILSON.†

The introduction of compressed air in general laboratory equipment has caused chemists to heat precipitates over the blast lamp to a greater extent than when the foot bellows was in general use. Much of this blasting is not only unnecessary but instead of increasing accuracy it tends to give inaccurate results, for not only is there greater danger of mechanical loss of the precipitate but, as has been shown by the Committee on Platinum Laboratory Utensils of the American Chemical Society,¹ even the best platinum loses weight in appreciable amounts at a temperature in the neighborhood of 1,200° C. This temperature can be obtained in a crucible with some blast lamps, while with others of apparently the same construction such high temperatures are not given.

It is almost a universal custom to blast lime, alumina, and silica to constant weight. That blasting is unnecessary for lime has been shown by Hillebrand,² and his conclusions that the heat of a Bunsen burner is sufficient for lime have been confirmed in this laboratory. He, however, prescribes blasting both silica and alumina, and with ordinary short periods of heating over a Bunsen burner, his conclusions as to the necessity of blasting are correct. Some preliminary experiments made on precipitated silica and aluminum hydrate, however, indicated that two or three hours at the highest temperature ordinarily obtainable with a good Bunsen burner were sufficient to reduce these substances to constant weight and it was deemed desirable to ascertain the necessary conditions for igniting them.

All of the work, described in this paper was done using the Washington city gas, which is mainly an enriched water gas mixed with some true coal gas. Various temperature measurements were made by inserting a thermo element through a hole in a platinum crucible cover, and it was found that at a point about 1 mm. from the bottom of a 15 cc. platinum crucible the ordinary types of Bunsen burners gave temperatures in the neighborhood of 950° C. Measurements were made, using old-style Bunsen burners (where the air supply is controlled by a collar and two holes at the base of the chimney) and a number of more modern types, having improved methods of controlling the air and gas supply. To the surprise of the experimenters there was practically no difference in temperature when different types of burners which are in common use were employed, the old-style Bunsen giving about the same temperature as modern types when of the same size. Similar experiments were made with Meker burners, and it was found that both large and medium Meker burners

gave the same temperatures in the crucible; that is, about 1,025° C., or about 75° higher than that obtained by an ordinary burner. The small size Meker burner gave a lower temperature than the ordinary burner, but it was evident that the flame from this small burner was not large enough to properly heat the size crucible used, and it would probably be equally efficient for a smaller crucible.

Under similar conditions blast lamps gave temperatures, varying very much more than the burners. Using different blast lamps, temperatures of from 1,075° to 1,260° C. in crucibles were obtained. Measurements of the flame temperatures by putting exposed thermo elements in the hottest part of the flames gave temperatures of from 1,250° to 1,290° C. for the ordinary type of burners, 1,300° to 1,320° C. for Meker burners, and 1,410° to 1,580° C. for blast lamps. The gas consumption per hour and the approximate temperature, 1 mm. above the bottom of a covered 15 cc. crucible, of the burners and blast lamp used in these tests were as follows:

Flames.	Gas consumption per hour. Cu. ft.	Approximate temperature 1 mm. above bottom of covered crucible. ° C.
Bunsen burner (E. & A. Universal)	7.25	950
Meker burner (medium size).....	5.13	1,025
Blast lamp	18.75	1,150

EXPERIMENTS WITH SILICA.

In order to eliminate as far as possible all errors except those due to heating, a quantity of silica was prepared by decomposing sodium silicate with hydrochloric acid, evaporating to dryness, digesting with hydrochloric acid, and washing by decantation. This material was heated at a temperature of 105° C. until it was apparently dry, but no attempt was made to dry to constant weight. Different portions of this powder were heated in various ways. Table I gives the results of twelve experiments which were conducted by heating the silica at the highest temperature obtainable with burners used, for 3 hours before the first weighing and then for 1 hour more over a burner, after which it was weighed and heated for 15 minutes over a blast lamp.

In all of the experiments in this work a clay cylinder about 4 ins. in diameter was set around the crucible. This radiator does not appear to raise the temperature at the bottom of the crucible but does probably give a more uniform temperature over the whole of the inside. Table II shows the results of four experiments conducted in the ordinary way; that is, the crucibles were heated to redness and then heated with the blast lamp for 15 minutes before first weighing. They were then heated for five minutes, weighed, and heated for another period of five minutes and weighed. In the odd-numbered experiments (1, 3, 5, etc.) the burner used was of ordinary type (E. & A. Universal); in the even-numbered (2, 4, 6, etc.), the medium-sized Meker burner was used.

*Circular U. S. Bureau of Chemistry. †Contracts Laboratory, U. S. Bureau of Chemistry.

¹J. Ind. Eng. Chem., 1911, 3, 686-691. ²U. S. Dept. Int., Geological Survey Bul. 422, p. 119.

Experiments 1 to 6, inclusive, in Table I were heated rapidly up to the maximum temperature that could be obtained with the burner used. The remaining experiments were heated up gently at the beginning, taking about 15 minutes to bring them up to the maximum temperature, and then held at this temperature for the periods indicated in the table. In all of the tests recorded in Table I and II the crucibles used were cleaned with sand between the experiments and weighed only at the beginning, the calculations being based upon that weight. The experiments were conducted in pairs, and a control crucible was heated for about three minutes to about the temperature of the crucibles containing the precipitates, placed in the desiccator with them, and weighed immediately after

up rapidly at the beginning it is probable that some material was lost here also. It will be noted that in the experiments recorded in Table I in no case except in the first experiment was there a loss of as much as a milligram after the first heating. The small changes in weight are no greater than apparent changes in weight of the same object at different times.

The results in Table I indicate that it is more difficult to get constant weight by heating to the temperature of a blast lamp as soon as the material has been heated up to bright redness than it is if all the heating is done at a lower temperature and for a longer time. The results in Table I indicated that nothing volatile was driven off after three hours heat-

TABLE I.—RESULTS OF EXPERIMENTS WITH SILICA
(Heated 3 hours, then 1 hour, followed by 15 minutes blasting.)

Experiment No.	Weight of material taken. Grams.	—Weight—						—Change in weight—	
		After 3 hours over burner.		After 4 hours over burner.		After 15 minutes blast, following 4 hours over burner.		During fourth hour of heating.	Due to blast.
		Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.	Mg.	Mg.
1	0.8774	0.7902	90.06	0.7828	89.22	0.7827	89.21	— .7	— 0.1
2	.7749	.6925	89.36	.6923	89.34	.6919	89.30	— .2	— .4
3	1.0356	.9286	89.70	.9284	89.68	.9284	89.68	— .2	.0
4	1.0762	.9573	89.95	.9571	89.93	.9571	89.93	— .2	.0
5	1.3341	1.1972	89.74	1.1972	89.74	1.1967	89.70	.0	— .5
6	1.2378	1.0878	87.88	1.0878	87.88	1.0878	87.88	.0	.0
7	1.0592	.9581	90.46	.9577	90.42	.9577	90.42	— .4	.0
8	.9914	.8976	90.53	.8973	90.51	.8971	90.49	— .3	— .2
13	.6939	.6284	90.56	.6283	90.55	.6283	90.55	— .1	.0
14	.7888	.7124	90.32	.7125	90.33	.7124	90.32	+ .1	— .1
15	.9178	.8309	90.63	.8302	90.55	.8301	90.54	— .7	— .1
16	1.0181	.9214	90.47	.9206	90.39	.9207	90.40	— .6	+ .1

TABLE II.—RESULTS OF EXPERIMENTS WITH SILICA
(Heated to redness, then blasted.)

Experiment No.	Weight of material taken. Grams.	—Weight—						Change in weight.	
		After 15 minutes blasting.		After 20 minutes blasting.		After 25 minutes blasting.		Between 15 and 20 minutes blasting.	Between 20 and 25 minutes blasting.
		Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.	Mg.	Mg.
9	1.1373	1.0307	90.61	1.0300	90.56	1.0300	90.56	— 0.7	0.0
10	1.1638	1.0622	91.26	1.0616	91.22	1.0615	91.21	— .6	— .1
11	.9352	.8473	90.60	.8457	90.43	.8443	90.28	— 1.6	— 1.3
12	1.0174	.9180	90.23	.9179	90.22			— .1	

weighing them. The control crucible was cleaned only once during the series. Before this cleaning its weights varied 0.6 mg., the lowest weight being 0.2 mg. below and the highest weight 0.4 mg. above the initial weight. These changes were evidently not due to loss of weight in the control, since the highest weight recorded was next to the last before cleaning, and the last weight was 0.2 mg. greater than the first weight. After the cleaning the maximum variation of this control crucible was 0.3 mg.

As would naturally be expected, the material used is not perfectly homogeneous and the percentages of silica found for the various periods of heating can be used only as pointing to probable mechanical loss of part of the silica. Experiment 1, for example, shows a loss of 7.4 mg. during the fourth hour of heating, but the low percentage indicates that some silica was lost (blown out of the crucible). Experiment 5 shows a very much lower percentage than the rest of the series, but as the first six experiments were all heated

ing over the burner, but as no attempt had been made to check possible changes in weight of the crucible during the individual experiments another series of tests was run later. The results of this series are recorded in Table III. A portion of the same lot of silica was used. The material had been kept in a screw-top jar with no particular precautions to guard against slight changes in the moisture content, so that the percentages in the results differ considerably from the earlier experiments. Since the results in Table I indicated that silica was reduced to constant weight in three hours heating, in most of the experiments recorded in Table III weighings were made at periods of one, two, and three hours and finally after 15 minutes over the blast lamp. After each experiment the crucible used was wiped out and weighed. As in the first series a control crucible was heated for about three minutes to about the temperature of the crucibles containing the silica, placed in the same desiccator, and weighed immediately after them. Twenty

weighings of this control crucible were made. The extreme variations in all of these weighings was 0.4 mg. An inspection of the weights of this crucible shows that the variations in weight were not due wholly to volatilization of the crucible, but were errors in weighing. Since the crucibles containing the silica were cleaned between the experiments the individual weighings are not given in the table but only the apparent change in weight from the beginning to the end.

EXPERIMENTS WITH ALUMINA.

The preliminary experiments that were made with aluminum hydrate prepared in large quantities and ground after drying in an air bath showed that this material could be ignited to constant weight without the use of the blast, but as the dried aluminum hydrate was ground before igniting it was thought that constancy in weight might not be obtained as easily by starting with precipitates actually obtained in analysis. Therefore, 16 determinations of alumina in ammonium alum were made. Table IV gives the summary of results of these experiments. All the re-

quired from 45 to 60 minutes. Covered crucibles were then placed in the full heat of the burners for various periods, which are indicated in Table IV. Clay cylinders were placed around the crucibles as in the experiments with silica and the burners used were the same as used in those experiments.

The odd-numbered experiments (1, 3, 5, etc.) were heated with the ordinary type of burner (Universal) and the even-numbered experiments (2, 4, 6, etc.) were heated with medium-sized Meker burners. The corrections which were made for a number of these determinations are given in Table 4. They were made by evaporating the filtrate from the first precipitation in platinum, igniting to drive off the ammonia salts, dissolving the residue in hydrochloric acid, and precipitating the alumina by the addition of a small amount of ammonia. These correction precipitates were ignited in another platinum crucible. After ignition the pair of crucibles used for determinations and the control crucible which was heated for about three minutes to approximately the temperature of the others were placed in the same desiccator and weighed

TABLE III.—RESULTS OF EXPERIMENTS WITH SILICA, SHOWING CHANGES IN WEIGHT OF CRUCIBLES.

Experi- ment. No.	Weight of material taken. Grams.	———Weight.———								Change in weight of crucible from begin- ning to end of experi- ment. Mg.	Weight of control.	
		After 1 hour over burner.		After 2 hours over burner.		After 3 hours over burner.		After 3 hours over burner and 15 min- utes over blast.			At be- ginning of ex- peri- ment. Mg.	At end of ex- peri- ment. Mg.
		Grams.	Per ct.	Grams.	Per ct.	Grams.	Per ct.	Grams.	Per ct.			
17	1.1421			1.0147	88.85	1.0145	88.83	1.0147	88.85	—0.3 }	16.0353	16.0351
18	1.0293			.9126	88.66	.9123	88.63	.9122	88.62	— .6 }		
19	.9746	0.8661	88.87	.8653	88.78	.8650	88.75	.8651	88.76	.0 }		
20	1.0235	.9096	88.87	.9086	88.77	.9085	88.76	.9083	88.74	— .6 }	16.0350	16.0350
21	.9278	.8227	88.67	.8220	88.60	.8220	88.60	.8219	88.59	— .1 }	16.0353	16.0352
22	1.0891	.9654	88.64	.9644	88.55	.9642	88.53	.9642	88.53	— .7 }		
23	.8091	.7181	88.75	.7179	88.73	.7175	88.68	.7174	88.67	— .4 }		
24	.9972	.8842	88.67	.8843	88.68	.8838	88.63	.8837	88.62	— .5 }	16.0350	16.0349
25	.8684	.7706	88.74	.7700	88.66	.7697	88.64	.7695	88.62	— .4 }	16.0350	16.0349
26	.7749	.6597	88.56	.6593	88.52	.6590	88.49	.6590	88.49	— .6 }		

agents used contained less than 0.5 mg. of non-volatile residue in 100 cc. All precipitates and boilings were made in platinum dishes. The material taken was dissolved in 25 to 30 cc. of water, 25 cc. approximately five times normal hydrochloric acid added, the solution made barely alkaline by the addition of five times normal ammonia, and boiled. Experiments 1 and 2 were washed only with water. In the others the washing was with faintly alkaline ammonium nitrate about one-fifth normal. In experiments 3 to 8, 11, 12, 15, and 16 macerated filter paper was added. After washing the precipitates, they were placed with the papers in crucibles, covered, and heated very gently, being held about 8 inches above the top of the flame until the papers began to smoke. The crucibles were then lowered to within about 5 inches of the flame and heated until all smoking had ceased and nearly all of the carbon was destroyed. They were then lowered until the flame just touched and heated the lower part to a dull red and held at this temperature until the carbon was burned off. The ignition to this point re-

after being kept there for about 15 minutes. The errors due to weighing seemed to be of about the same magnitude as those in the silica determinations, the second weight of the control crucible varying from —0.5 mg. to +0.3 mg. from the first weight.

After each experiment the precipitate was brushed out of the crucible and the crucible weighed. Since the crucibles used for igniting the alumina were cleaned between the experiments the individual weights are not given, but only the difference between the weighing before and after the experiment. These differences vary from +0.6 mg. to —0.6 mg. The control crucible was cleaned before experiments 7, 9, 11, and 13. The weights and calculations given in Table 4 are all based upon the weight of the crucible at the beginning of the experiment. The losses in weight from the initial weighing of the ignited alumina for the final weighing in only a very few cases amount to as much as 1 mg. and in no case to as much as 2 mg. These experiments, as the experiments with silica, indicate that in weighing a platinum crucible under con-

ditions of analysis, the error in weight may amount to as much as a milligram if not more. It therefore appears that heating alumina in the manner indicated for three or four hours over a burner reduced it to a constant weight within the limit of accuracy of such a determination.

All weights throughout this whole series of experiments were made using an accurately standardized set of weights. The weights of 1 gram and upward were lacquered brass and the fractional weights were platinum. An error of as much as a milligram made in weighing a 15 cc. platinum crucible is apparently due to condensation on the surface of either crucible or the weights or both. It seems to be illogical to assume that all these errors are due to condensation on the surface of a platinum crucible and not on the lacquered brass weights. The writers have observed the same apparent difference in the weight of a platinum crucible which was kept in a balance case under exactly the same conditions as the weights, and it is certainly reasonable to suppose that a piece of bright platinum would be less subject to variations in condensation on its surface than lacquered articles of like weights.

It is the custom in some works' laboratories to brush precipitates such as silica from the crucible on to a balanced watch glass for weighing, thus saving the time used in weighing the crucible. The method of weighing the crucible and then weighing the crucible with the precipitate is generally considered more accurate and is, of course necessary for such substance as lime, but it is very doubtful whether this method of weighing is really as accurate as the method of transferring the precipitate to a balanced watch glass, where the weight would be much smaller and the error would be only that due to error in weighing the precipitate itself, and not the relatively large error which is due to weighing a heavy crucible. An assayer would not think of weighing his annealing cup with the gold in it and then weighing the empty annealing cup and getting the gold by difference, and it is probable that, for substances like alumina and silica, weighing after the manner of the assayer would be conducive to more accurate results than by following the regular method.

This is aside, however, from the object of this paper. An attempt has been made to determine whether alumina and silica can be ignited to constant weight without the use of a blast lamp, and as a result the authors are of the opinion that with slow initial ignition and final heating at the highest temperature that can be obtained with a burner, silica is practically always reduced to constant weight in two hours and generally in one hour. Alumina requires a somewhat longer period. About three hours reduces the weight to within the limit of error of the determination.

New cement works to produce 1,000 bbls. a day have been opened on the Manchester ship canal.

TABLE IV.—RESULTS OF DETERMINATIONS OF ALUMINA IN AMMONIA ALUM.

Experiment No.	Change in weight of crucible during experiment. Mg.	Weight of control crucible at beginning of experiment. Grams.	Weight of control crucible at end of experiment. Grams.	Change in weight of crucible during experiment. Mg.	Weight of alum taken from ammonia		Alumina after 3 hours over burner.		Alumina after 4 hours over burner.		Alumina after blasting 4 hours over burner.		Alumina after slow ignition (about 45 minutes) and 15 minutes blasting.		Alumina after slow ignition (about 45 minutes) and 25 minutes blasting.		Correction. Mg. Per ct.	
					Grams.	Per ct.	Mg.	Per ct.	Mg.	Per ct.	Mg.	Per ct.	Mg.	Per ct.	Mg.	Per ct.	Mg.	Per ct.
1	()	16.0469	16.0469	0.0	1.3735	11.08	152.1	11.08	152.4	11.10	151.4	11.02	174.5	11.44	173.7	11.39	()	()
2	()	16.0468	16.0468	0.0	1.1831	11.27	133.3	11.27	132.9	11.23	132.7	11.22	139.6	11.25	139.5	11.24	()	()
3	-0.3	16.0468	16.0468	0.0	1.6159	11.32	183.4	11.35	183.4	11.35	181.6	11.21	194.5	11.47	193.9	11.42	0.5	0.03
4	()	16.0468	16.0468	0.0	1.4555	11.32	164.7	11.32	163.5	11.23	162.9	11.19	174.5	11.44	173.7	11.39	()	()
5	+1.1	16.0468	16.0468	+2	1.3985	11.48	160.6	11.48	160.3	11.46	159.5	11.41	174.5	11.44	173.7	11.39	0.0	0.00
6	()	16.0468	16.0468	0.0	1.0286	11.16	114.8	11.16	114.4	11.12	114.5	11.13	139.6	11.25	139.5	11.24	0.0	0.00
7	-1.6	16.0464	16.0461	-3	1.2434	11.28	140.3	11.28	140.1	11.27	140.0	11.26	174.5	11.44	173.7	11.39	1.8	0.17
8	()	16.0464	16.0461	0.0	1.0681	11.15	118.0	11.15	118.0	11.15	117.8	11.13	139.6	11.25	139.5	11.24	0.2	0.02
9	()	16.0444	16.0439	-5	1.8721	11.22	209.7	11.20	209.7	11.20	208.7	11.15	194.5	11.47	193.9	11.42	1.1	0.06
10	()	16.0444	16.0439	0.0	1.5296	11.28	172.5	11.28	171.9	11.24	171.4	11.21	194.5	11.44	193.9	11.42	0.6	0.04
11	()	16.0425	16.0426	+1	1.5260	11.28	172.5	11.28	171.9	11.24	171.4	11.21	194.5	11.44	193.9	11.42	0.0	0.00
12	()	16.0425	16.0426	+1	1.2408	11.08	152.1	11.08	152.4	11.10	151.4	11.02	174.5	11.44	173.7	11.39	0.0	0.00
13	()	16.0415	16.0418	+3	1.3264	11.47	162.1	11.47	162.1	11.47	161.5	11.42	194.5	11.44	193.9	11.42	0.0	0.00
14	()	16.0415	16.0418	+3	1.2361	11.27	139.3	11.27	139.3	11.27	139.0	11.25	194.5	11.44	193.9	11.42	0.0	0.00
15	()	16.0419	16.0419	0.0	1.4354	11.51	164.7	11.51	164.7	11.51	163.9	11.42	194.5	11.44	193.9	11.42	0.0	0.00
16	()	16.0419	16.0419	0.0	1.3556	11.37	154.2	11.37	154.2	11.37	153.8	11.35	194.5	11.44	193.9	11.42	0.0	0.00

¹ Not determined.

THE CARBIDE METHOD OF DETERMINING MOISTURE.

By HAROLD A. DANNE.

The above process was first made public by me before the Society of Chemical Industry of Victoria, at a meeting held under the presidency of Prof. Orme Masson, of Melbourne University, Australia, and published in the records of the society of Chemists & Druggists of Australasia, of January 7, 1901, and was as follows:

"A Direct Method of Estimating Minute Amounts of Moisture," by Harold A. Danne.

"The method, for there is only one, given by Thorpe for the estimation of moisture, namely that of the

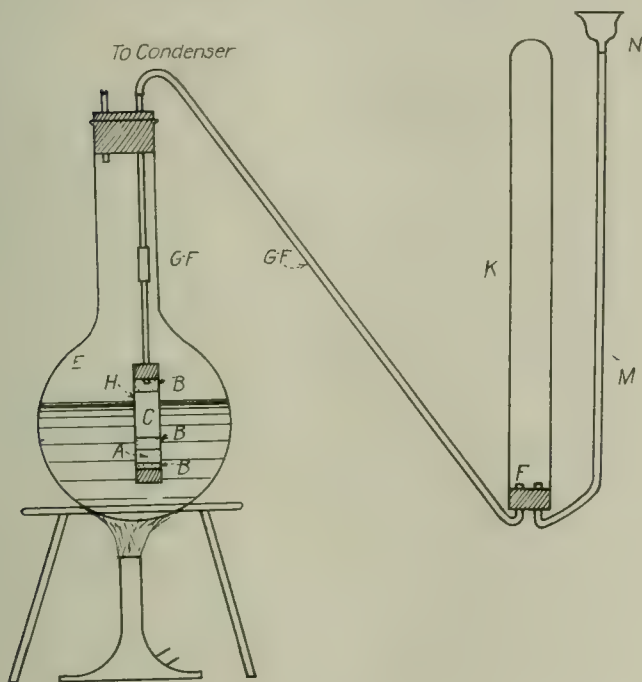


Fig. 1—Apparatus for Carbide Method of Determining Water.

A, substance to be tested; B, cotton plugs; C, powdered carbide; D, rubber plugs; E, flask; FG, gas delivery tube; H, tube for loading with carbide and sample; K, gas collection tube (graduated); MN, reservoir for collecting surplus water and adjusting pressure to atmospheric.

drying loss, is open to this objection, that in the presence of other volatile constituents, its only moderate value is reduced still further. Under these conditions the analyst is directed to estimate these 'other volatile' portions somehow and then again the moisture by difference. As from many causes this latter process is always more or less unsatisfactory, other methods were sought and the following adopted. Briefly put, the moisture is estimated by the amount of acetylene gas, evolved in interaction of its vapor with an excess of calcium carbide as in the equation— $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + 2\text{H}_2$.

The apparatus is as follows:

The carbide tube is about 3 ins. in length by $\frac{1}{2}$ in. in diameter and is plugged at one end, the other being provided with a rubber stopper pierced for a gas delivery tube. This carbide tube is charged specially for

special substances. For a test experiment on a weighed quantity of water about $\frac{1}{2}$ in. of cotton wool is first inserted and then about 2 drops of distilled water weighed in another plug of wool is then inserted and the tube is filled to within $\frac{1}{2}$ in. of the upper stopper with a well powdered and mixed crystalline carbide. The stopper is then inserted with an upper plug of wool and the delivery tube connected. This tube carries the gas evolved through a drying tube filled with calcium chloride to a eudiometer, where it is collected over acetylene saturated water. A movable tube is provided to allow the level of the liquid in the eudiometer to be adjusted at the end of the reaction and the reading thus made at atmospheric pressure. This proceeds slowly in the cold, and it is better to hasten it by the introduction of the generator tube into a flask water bath kept at 200°F . Under these conditions the reaction will be complete in from 10-15 min. A blank experiment is to be made and the result deducted from all subsequent estimations.

Other precautions to be adopted are: The wool is to be taken from a stock kept in a dryer. The time of reaction should be about the same. The same sample of carbide is to be used after a standard is reached. Following are some results:

Experiment.	Reading.	Temp. of React.	Time.
1	28 cc.	60	10 min.
2	29 cc.	60	15 min.
3	28 cc.	60	10 min.

Thus the blank or tare of the apparatus was found to be 28 cc. With these precautions, a series of estimations with known water came out as follows:

Water.	Mm. C_2H_2 corrected.	Mm. per mgm. H_2O .
145	351	2.240
161	299.5	2.419
150	363	2.420

An average of 2.42 mm. per mgm. was found to give very concordant results and was finally adopted under these conditions. The utility of the process extends to the following: Whole or powdered plants, alcohols, ethers and their mixtures; water of crystallization substances to be avoided are those containing the halogens in loose combination—the mercuric salts.

The silicuretted hydrogen evolved causes the water, in time, to become clouded.

The value of the process mainly seems to be:

- 1st. Its direct nature is more scientific.
- 2nd. A greater number of estimations may be accomplished in a given time.
- 3rd. The comparatively large volume of gas evolved ensures a higher per cent of accuracy.
- 4th. It is thoroughly a *commercial analytical* method.

This process was not publicly acted upon until four years afterward, when Mr. Frederick Stone, City Analyst of Melbourne, pointed out to me an article by P. V. Dupré on the subject, claiming originality. I wrote to Dr. Dupré fully, enclosing a copy of my original investigation, and received no answer. I, however, had installed the apparatus at several laboratories, notably in the Melbourne University, at the request of Dr. Masson, for general and special uses and

also in the Government Explosive Testing Laboratories for use on cordite, etc. The following year I visited London, England, but learned, on calling at Dr. Dupré's office to see him about the matter, that he had died that morning and his office was closed indefinitely. I did not, therefore, pursue the matter any further.

The process as originally read before the Society gave details of the treatment of such substances as insect powder (*folii pyrethri rosacei*), which was previously supposed to contain a volatile oil, actively poisonous to insects on account of its volatility, but which, by this method, was shown to have a drying loss practically identical with the moisture shown to be present when treated by the carbide method. Its content, therefore, was shown to be nonvolatile under 100° C.

The paper also mentioned the treatment of powdered drugs, including spices, and also went on to describe tests on substances containing water of crystallization, differentiating the marked period of dissociation of the adherent moisture from that of the water of crystallization. This latter fact was mentioned, as it was very striking when demonstrated. The gas developed by the adherent fortuitous moisture wholly ceased to bubble up through the eudiometer some minutes before the gas due to the water of crystallization.

To have the carbide in contact with the substance always seems to me to involve the risk of chemical interaction with its own products, such as saponification, and, indeed, in my own experiments, results proved this to be the case. Furthermore, there is no necessity to so admix the charge, as, with a little ingenuity, they can be kept separate. If, however, it is found necessary to mix other substances with the sample so that it may be dehydrated completely, it is wise to pay very particular attention to the blank tests or tare of the other substances and the apparatus, as I called it originally, and too much importance cannot be put on this feature to get it constant by the use of standardized articles and procedure, so that the only uncertain portion is the moisture to be determined, the quantity of gas developed per mgm. H_2O is relatively very large, that being one of the reasons which led to my developing this method, and even a difference in quality of cotton or india rubber plugs being touched by the finger, will interfere with the accuracy of determination.

In all cases the greatest care should be exercised that no accidental moisture on the interior of stoppers, etc., is permitted.

Enclosed is a chart of the apparatus originally used by me after many experiments. The flask is provided with water or glycerine and water, so as to maintain a steady temperature at 90° C. in the loaded tube. This tube is open at both ends for convenience in quick loading, such quick loading being most desirable to insure the absence of accidental moisture other than

that in the sample. It also seemed to me important that the sample should have free circulation of the atmosphere inside the tube, so as to be quickly and completely dehydrated. I am also of the opinion that the space occupied by the sample and carbide should be as restricted as possible for the same reasons; therefore, in my final results, I always loaded the tube from the bottom, in the following order:

1. Perforated plug, perforated for the gas delivery tube.
2. Standardized cotton plug.
3. Powdered standardized carbide, powdered to no finer than 40 mesh powder.
4. Plug of standardized cotton.
5. Sample of weighed quantity of water.
6. Plug of standardized cotton.
7. Solid bottom plug.

I did not find it at all necessary to interfere with the temperature of the eudiometer with its enclosed gas, simply making a reading of the water and the surrounding atmosphere and correcting the value of the gas to suit at reading, as is done in all gas analyses.

Going over the results of Mr. H. C. McNeil, of the Contracts Laboratory, U. S. Department of Agriculture, it is my opinion that if one used the same water over and over again for the work, it becomes so saturated with acetylene that at average temperature there is practically no variation, due to solubility of the acetylene in common distilled water. With regard to the plugs of cotton described by him, it should be standardized, as I have said before, as it is a well-known fact to those who handle cotton that it is very irregularly hygroscopic, and this will interfere with the accuracy of the test if not attended to.

It was suggested by Prof. Masson, at the original meeting where the process was discussed by the chemists present, that Moisson's pure crystallized carbide could be used to advantage, and that would be so if it could be obtained commercially as ordinary carbide can.

It has to be also remembered that resulting hydrate of lime has chemical action of its own, both upon the moisture present and upon the other substances with which it is in contact, so that to avoid this complication I should think it preferable to avoid intermixture of the carbide and the sample. Particularly with oleic acid, it must be obvious that the lime will form the hard oleate cake mentioned. Stearic acid would have the same objection, as would linseed oil, on which Mr. McNeil has noted, "It causes much foaming."

In conclusion I wish to say that I fully agree with Mr. McNeil in his statement that this method has possibilities that warrant a further and fuller study of its utility and varied uses, especially when it is remembered that it is the only process for determining, analytically, these minute amounts of moisture, which can command the confidence of the scientific analyst.

This season's English hop crop is estimated at only 33,000,000 lbs.

DETERMINATION OF LITHIUM.*

By LESLIE RUSSELL MILFORD.

In the work with the first samples of the Saratoga mineral waters, which the writer has been analyzing, the determination of lithium was found to be difficult and the results obtained were not satisfactory because of the fact that parallel determinations would not check and too small volumes of water had to be used.

The waters of these springs are highly mineralized, the chlorides ranging from 100 to 11,000 parts per million. Therefore, a great deal of trouble was experienced in volatilizing the ammonium salts when working with large volumes of water. Mechanical loss, due to decrepitation and splitting apart of the crystals, was a constant source of error. On the other hand, if one took a small volume of water the chlorides could be dried and the ammonium salts driven off more easily, but the possibility of multiplying errors would be great because of the relative small amounts of lithium present.

The need of an improvement or change of the method given on page 29, Bulletin 91, of the Bureau of Chemistry¹ became apparent. By consulting the literature and various solubility tables² and studying the methods of Gooch,³ Treadwell,⁴ Kennicut,⁵ Frenkel,⁶ and Rammelsberg,⁷ the following procedure was adopted whereby a larger volume of water could be used and a residue obtained which would give, when treated, a lithium salt containing only a spectroscopic trace of sodium and potassium.

Method.—Two hundred to five hundred cc. of the water are evaporated to dryness in a large platinum dish with the occasional addition of small amounts of concentrated hydrochloric acid. After all of the water has been evaporated to dryness the dish and contents are heated at 120° C. for about 30 minutes to dehydrate the silica. The residue is then treated with a little dilute hydrochloric acid, just enough to moisten the contents of the dish. Then about 25 cc. of 95 per cent alcohol are added and the residue is rubbed up with a small pestle until all lumps and crystals are crushed. The alcoholic extract is then poured on an 11 cm. quantitative filter and the filtrate caught in another platinum dish. The residue is washed with 95 per cent alcohol until it shows no lithium line when examined in the spectroscope. The alcoholic filtrate and washings are united and evaporated on the water bath. When all of the alcohol has evaporated some dilute hydrochloric acid is added to the contents of the dish, and the whole evaporated to dryness and then the residue rubbed up with absolute instead of 95 per

cent alcohol. The filtrate is caught as before in a platinum dish and the residue on the filtrate washed with absolute alcohol until no lithium line is seen when tested from time to time with the spectroscope. The alcohol is evaporated and the dry residue taken up with a little dilute hydrochloric acid. Calcium hydrate is added until the solution is alkaline. The magnesium is precipitated as the hydrate and the solution is filtered. To the filtrate add ammonium hydrate and ammonium oxalate to precipitate the calcium. This is allowed to stand twelve hours or over night when it is filtered off. The calcium oxalate precipitate must be thoroughly washed (usually about 100 cc. of water is sufficient), as lithium is held relatively fast by the precipitate and does not wash out easily. When the residue no longer shows lithium, as verified by the spectroscope, the solution is evaporated to dryness and the excess of ammonium salts driven off by first heating the dish on a radiator, then over the free flame. The residue in the dish is taken up with a little dilute hydrochloric acid heated, and ammonia and ammonium oxalate are again added to precipitate any calcium which might be present. In any case the solution is filtered from any calcium or magnesium that precipitates on concentrating the solution. The filtrate is evaporated to dryness and all ammonium salts are driven off by heating in platinum to a little below redness. The residue is again taken up with water, filtered, and washed (using as little wash water as possible), then evaporated to dryness and heated in platinum to a little below redness to drive off any ammonium salts. All of the calcium and practically all the magnesium have now been removed, and there is left a residue containing lithium chloride with traces of sodium and potassium chlorides. If we have iodides and bromides present, this residue will contain small amounts of these substances because they are more soluble than the chlorides. In order to insure a residue consisting of chlorides only we treat the contents of the dish with a little dilute hydrochloric acid and chlorine water, evaporate to dryness, and gently ignite. By this we have replaced the iodine and bromine with chlorine.

The residue is now taken up with a little water and treated with a few drops of dilute hydrochloric acid and transferred to a large platinum dish.

About 30 cc. of amyl alcohol are added and the contents of the dish brought to boiling with constant rapid stirring when heating to minimize the bumping caused by the escape of the water. When all of the water has evaporated, the dish is placed on the steam bath and a drop of dilute hydrochloric acid added to reconvert small amounts of lithium hydrate to the chloride. The evaporation is continued until the volume reaches about 15 cc. The amyl alcohol is then filtered into a platinum dish and evaporated to dryness. Water and a few drops of dilute sulphuric acid are now added and the contents of the dish again evaporated to dryness. The excess of sulfuric acid is removed by heating the dish over a radiator and then over the direct flame to dull redness. The dish is cooled, the contents dis-

*From the Journal of Industrial and Engineering Chemistry.

¹ and ² "Mineral Waters of the United States," U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin 91, 1906.

³Atherton Seidell, "Solubilities of Inorganic and Organic Substances," 1907.

⁴ and ⁷ Treadwell-Hall, "Analytical Chemistry," 1911.

⁵Chamot-Redfield, "Analysis of Water for Household and Municipal Purposes," 1911.

⁶M. Frenkel, D. Sc., "Extract From the Records of Medical Hydrology and Climatology," Paris, Dec., 1903.

solved in water and a few drops of ammonium hydrate are added to precipitate the last trace of magnesium which is invariably present at this stage. Filter, wash with boiling water, evaporate to dryness, free from ammonium salts, and repeat previous process till no more magnesium precipitates on addition of ammonium hydrate. Finally filter into a weighed platinum dish, evaporate to dryness, burn, cool in a desiccator, and weigh as lithium sulphate. From this result we subtract 0.0017 gram to correct for the solubility of the sodium and potassium chlorides in amyl alcohol, their presence having been verified by the spectroscopic.

The contents of the filters containing the NaCl, KCl, etc., which were taken out by the 95 per cent alcohol and absolute alcohol together with the contents of the platinum dish and filter from which the amyl alcohol has been driven off, are all dissolved in water, united, freed from other salts and made up to a definite volume. By using aliquot portions we can determine sodium and potassium by Gooch's method. Or the usual procedure, using a small portion of the silica filtrate, can be followed.

Advantages Given by This Modification.—(1) Waters high in chlorides can be handled with ease with no danger of loss of lithium by decrepitation.

(2) Large volumes of water can be used, thus reducing the error when computing to milligrams per liter.

(3) The results can be found to check and can be obtained much more quickly by having a residue free from an excess of sodium and potassium chlorides.

(4) The method involves the use of calcium hydrate instead of barium hydrate for the precipitation of magnesium. This procedure does not introduce another substance which has to be removed by ammonia and ammonium oxalate because we have our calcium in common and have a precipitate of calcium oxalate which is less soluble and more easily washed than barium oxalate.

Prospecting with drills at the state coal mine in Victoria, Australia, has shown that there are 22,000,000 tons of coal in a bed 2 ft. 6 ins. thick, covering 3,500 acres. Eleven shafts have been sunk, ranging in depth from 177 to 283 ft., but all are not producers, only 3, 5 and 11 being used for that purpose at present. In 1911, 710,058 tons of coal were mined, but with the exception of slack coal, which averages 42 per cent of the output, no coal was sold to the public. Evidently public utilities are run by the Government or else they have to buy this coal from the Government, for the prices given at the mine are \$2.75 for screened coal, \$2.50 for second grade, \$2.12 for run of mine, and \$1.62 for slack. The total number of men employed at the mines near Wonthaggi are 1,200; these averaged \$3.47 per shift during 1911 when working on contract.

A NEW APPARATUS FOR THE VOLUMETRIC DETERMINATION OF CARBON DIOXIDE.*

By HOWARD W. BRUBAKER.

In the Journal of Industrial and Engineering Chemistry for March, 1912, appeared an account, by L. T. Bowser, of a volumetric method for the determination of carbon dioxide. In this method the carbon dioxide is liberated and then absorbed in a solution of potassium hydroxide. This solution is washed into a 100 cc. graduated flask, water added to the mark and an aliquot titrated, using phenolphthalein as the indicator to the disappearance of the red color, then methyl orange, the second part of the titration indicating the amount of carbon dioxide in the solution.

The writer had occasion to try out the method to see whether it could be used by a class of comparatively inexperienced students of chemistry. As a result of a little experience with the method some objectionable features were found with the apparatus used by Mr. Bowser which make it impracticable for use by students. Probably the most objectionable feature is the necessity of washing out the potassium hydroxide from the tall absorbing cylinder into a measuring flask. This process requires skilled manipulation, especially since it is necessary to wash the cylinder thoroughly and yet keep the whole volume of liquid and wash water down to 100 cc., which seems advisable, in order that a sufficiently large fractional portion of the solution may be titrated without using a very large volume.

Another objection lies in the fact that at the end of the decomposition of the carbonate when an attempt is made to distill over some of the liquid, in order to drive the last portion of carbon dioxide into the absorbing cylinder, there is a tendency for the potassium hydroxide solution to suck back into the condensing apparatus. In order to overcome these objections and to make the method applicable for the use of inexperienced students the writer devised the apparatus shown in the accompanying figure.

B is a standardized Erlenmeyer flask holding 100 cc. when filled to the mark.

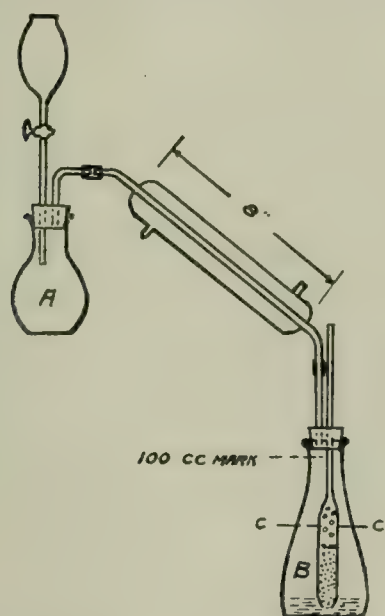
C is a 10 cc. pipette half filled with glass beads, having a coil of copper wire at the bottom to prevent any of the beads from becoming wedged into the tapering part of the tube.

Eight cc. of the potassium hydroxide solution (50 grams KOH in 100 cc. water) are placed in the flask B which is then connected with the condenser as shown in the figure.

One gram of the material to be analyzed is placed in the flask A with about 50 cc. of water. The hydrochloric acid is run in from the funnel, drop by drop, until sufficient has been added to decompose the sample.

*From the Journal of Industrial and Engineering Chemistry

The carbon dioxide distils into the flask B, forcing the potassium hydroxide solution up into the pipette until it stands near the top of the broad portion where the bubbles break. There is left a thin layer of potassium hydroxide covering the bottom of the flask. The carbon dioxide which is not absorbed by this layer of potassium hydroxide passes up through the liquid in the pipette and is completely absorbed. After adding the hydrochloric acid the liquid in the distilling flask is heated and finally boiled for five minutes, the steam condensing and falling into the flask B. As can be seen by the construction of the apparatus, there is no backing up of the potassium hydroxide solution into the condenser even when the flame is entirely removed. This boiling drives the residual carbon dioxide into the absorbing flask where it is completely absorbed. If there is any doubt as to the last portion of carbon dioxide in the flask B having been absorbed, the flask is shaken for a minute or two after disconnecting it and



Apparatus for Carbon Dioxide Determination.

while holding a finger over the opening of the glass tube.

After distilling steam over for five minutes the writer has always found the carbon dioxide to have been completely absorbed.

The stopper with the pipette is now partly withdrawn from the flask B, the pipette rinsed out several times into the flask and water added to the 100 cc. mark. After mixing, a 25 cc. portion is taken for titration. The advantages of this apparatus are as follows:

1. Ease of construction.
2. Ease of manipulation.
3. It permits of distilling over as much of the liquid as desired, to drive out the residue of carbon dioxide, without experiencing any annoyance due to sucking back of the potassium hydroxide solution into the condenser.
4. It eliminates the necessity of transferring the alkaline solution to another vessel before making it

up to a definite volume, thus also keeping it away from contact with the carbon dioxide of the air.

The following table shows some results obtained with the apparatus here described.

Sample.	CO ₂ Found.	Per cent.
Na ₂ CO ₃	By direct titration.....	39.40
Na ₂ CO ₃	By distillation and titration:	
Na ₂ CO ₃	1st run.....	39.40
Na ₂ CO ₃	2nd run.....	39.45
Baking powder No. 1	Available CO ₂ , 1st distillation...	8.10
Baking powder No. 1	Available CO ₂ , 2nd distillation...	8.02
Baking powder No. 1	Available CO ₂ , 3rd distillation...	8.10
Baking powder No. 1	Total CO ₂ , 1st distillation.....	11.01
Baking powder No. 1	Total CO ₂ , 2nd distillation.....	10.91
Baking powder No. 2	Available CO ₂ , 1st distillation...	8.76
Baking powder No. 2	Available CO ₂ , 2nd distillation...	8.62
Baking powder No. 3	Available CO ₂ , 1st distillation...	10.74
Baking powder No. 3	Available CO ₂ , 2nd distillation...	10.91
Limestone	Gravimetric method.....	40.25
Limestone	Volumetric, 1st titration.....	40.23
Limestone	Volumetric, 2nd titration.....	40.40

When the method is used for the determination of the available carbon dioxide in baking powders, where it is necessary to decompose the sample with water, frothing occurs during the heating of the solution. This makes it difficult to distil over enough water to drive out the last of the carbon dioxide. In order to overcome this difficulty, when the distillation was carried as far as was practicable, the distilling flask was filled with water through the dropping funnel, thus forcing any carbon dioxide into the absorbing flask.

By using a solution of 25-30 per cent alcohol instead of pure water, for decomposing the baking powder, it was found possible to prevent excessive frothing.¹ One could then clear the flask of the last portion of carbon dioxide by distilling over a little of the liquid and thus do away with the necessity of filling the flask with water.

It is necessary to determine the carbon dioxide in the potassium hydroxide solution used as the absorbing reagent and to apply the correction in each titration.

In the writer's experience with the volumetric method for carbon dioxide the greatest source of error is in the titration. The end point with phenolphthalein must be approached with care as the disappearance of the red color is rather slow.

The value of the brick, tile, sewer pipe, pottery and various other clay products made in Missouri in 1911, according to the United States Geological Survey, was \$6,274,353. This is a decrease of about \$750,000 compared with the figures for 1910.

The Belgium consul at Yokohama states that the total production of copper in Japan in 1911 amounted to 51,708 tons, valued at \$13,460,000 United States gold, being an increase of 2,562 tons and \$559,500 over the production in 1910, and an increase of 13,374 tons as compared with 1909. More than half the copper is from the Ashio, Besshi and Kosaka mines. The Hidate mine is also making great progress, and turned out 5,674 tons last year, or more than seven times the quantity produced in 1907.

LIQUOR SODII PHOSPHATUS COMPOSITUS U. S. P.*

By MITCHELL BERNSTEIN, P. D.

Relative to this pharmacopœial preparation many formulas and suggestions have been offered. The writer conducted a series of experiments using both the U. S. P. and many suggested modifications and formulas. In this connection, each formula in turn was wanting in some respect or other.

In view of preventing the crystallization of Sodium Phosphate, it was thought that Anhydrous Sodium Phosphate might solve the difficulty. Various samples of so labeled dried, exsiccated and anhydrous Sodium Phosphate were obtained from reputable wholesale houses. When examined, however, each respective sample showed a deficiency of Sodium Phosphate. Thus in one case was found 40.5 per cent water. In another case 17.5 per cent water of crystallization.

It is evident that if these salts were used in making the solution, after we had calculated on an Anhydrous salt, that we surely would have a brilliant preparation, but one in which we would not have the corresponding amount of uneffloresced Sodium Phosphate.

A perfectly anhydrous sodium phosphate was made by the writer, according to the U. S. P. This was ascertained with surety. The method of preparing the compound solution of Sodium Phosphate was as follows:

Dissolve the sodium nitrate and exsiccated sodium phosphate together with the citric acid in a flask by means of heat of a water bath. Then make volume up to 1,000 cc. Filter while warm into a sterile container.

The use of the exsiccated sodium salt appears very satisfactory, for in the many preparations made using the exsiccated salts no crystallization has ever occurred.

Several preparations have been kept under observation for a little over three years to date, having used the 4 per cent sodium nitrate and 13 per cent citric acid in the preparation as per U. S. P. together with the proportional amount of sodium phosphate exsiccated, corresponding to 1,000 gms. sodium phosphate. During the three years the preparations have been exposed to varying temperatures, varying from 30° F. to 95° F. The preparations still remain clear, colorless and sparkling; never having even shown signs of crystallization at as low as 30° F. and still free from any fungous growth, which is always manifest after the U. S. P. preparation remains standing for some time.

In conclusion the writer would suggest the use of

	Per cent.	Grams.
Sodium nitrate.....	4	40
Citric acid.....	13	130
Anhydrous sodium phosphate.....		396.6
(Equivalent to 1,000 gm. sodium phosphate.)		
Distilled water to make, c.c.....		1,000

*From the American Journal of Pharmacy.

Add the citric acid and sodium nitrate to 150 cc. of distilled water contained in a flask, then add the anhydrous sodium phosphate. Dissolve by the aid of heat of water bath. Make volume up to 1,000 cc. and filter while warm into a sterilized container—stoppered with a sterile plug of absorbent cotton.

When made as above, we obtain a preparation, which, as has been stated, is clear, colorless, sparkling and permanent and representing the U. S. P. amount of sodium phosphate in this preparation.

Preliminary statistics issued by the U. S. Geological Survey show that the smelter production of primary copper in the United States in 1911 was 1,097,232,749 lbs., as compared with 1,080,159,509 lbs. in 1910, an increase of about 1.5 per cent. The production for 1911 was the largest in the history of the industry. The total production of new refined copper in 1911 was 1,433,875,026 lbs., exceeding that of 1910 by 11,835,893 lbs. Secondary copper was produced by regular refining plants to the amount of 31,040,874 lbs. in 1910 and 27,896,727 lbs. in 1911. In addition to the secondary material treated by the regular refining companies, plants that treated secondary material exclusively produced a total of 186,311,000 lbs. (figures subject of revision) of copper as copper and in brass and other alloys of copper, making a total production of 214,207,727 lbs. from secondary sources. Of this total, at least 62,000,000 lbs. were produced by remelting clean scrap produced in the process of manufacture of copper and brass articles. If the output of plants treating purely secondary material is added to the production of the regular refining companies, the contribution of the United States to the world's supply of copper for 1911 is found to be 1,648,082,753 lbs.

The total quantity of domestic fluorspar reported to the U. S. Geological Survey, as marketed in the United States in 1911 was 87,048 short tons, compared with 69,427 short tons in 1910, an increase of 17,621 short tons. The production in 1911 was the largest ever recorded, 62,825 short tons of domestic gravel spar being marketed, against 52,013 short tons in 1910. The highly satisfactory condition of the fluorspar industry in 1911 was due partly to the ability of American producers to meet the demand more nearly than heretofore and to produce a better and more uniform grade of gravel spar than can be obtained by importation, and partly on account of the import duty of \$3 per ton. Fluorspar is used in the manufacture of glass and of enameled and sanitary ware, the electrolytic refining of antimony and lead, the production of aluminum, the manufacture of hydrofluoric acid, and in the iron and steel industries, where it is used as a flux in blast furnaces and in basic open-hearth steel furnaces. It is estimated that about 80 per cent of the American fluorspar output, mainly in the form of gravel spar, is consumed in the manufacture of basic open-hearth steel.

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NOTES AND COMMENTS.

Canadian Standards for Turpentine.

The following standards for turpentine have been put in force in Canada under the Act respecting the adulteration of food and other articles:

When turpentine is sold as a drug, for medicinal purposes or to the order of a physician, it shall meet the pharmacopœial requirements as provided by section 7 of the Act.

When turpentine is sold under any other conditions than for purposes of medicine, as above, it shall meet the following requirements: It shall be entirely free from mineral oil; unless sold as wood turpentine, it shall absorb not less than 340 times its weight of iodine (Hubl solution and method); if sold as wood turpentine, it shall absorb not less than 240 times its weight of iodine by the same method; the undissolved (unpolymerised) residue on treatment of 10 cubic centimeters with 40 cubic centimeters of a sulphuric acid containing 20 per cent of the fuming acid, shall not exceed 10 per cent by volume of the sample; the refractive index of this residue shall be not less than 1.4950 at 20° C.; the refractive index of the sample at 20° C. shall lie between 1.468 and 1.473; the specific gravity of the sample at 20° C. shall not be less than

0.86; the initial boiling point shall not be lower than 150° C. under ordinary atmospheric pressure; at least 75 per cent by volume shall distil below 160° C.; the residue on evaporation over a steam bath shall not exceed 2 per cent.

German Nitrate Production Versus Swedish.

For some years a group of houses, including the Badische Anilin und Soda Fabrik, have been producing saltpetre from the atmosphere and obtaining therefrom nitrate. According to the *Cologne Gazette*, the German producers of nitrates have found it impossible to continue competition with this group any further, at all events at a profit, and as a consequence some days ago it was decided to dissolve the syndicate of German nitrate manufacturers.

Extension of Canadian Cyanamide Works.

The American Cyanamide Co. of Niagara Falls, Ont., is making extensions to its plant, which, when completed, will cost about \$500,000 and will more than double the present capacity of the concern. The company is engaged in the manufacture of atmospheric nitrogen by the Frank and Caro process, the power being derived from the Niagara Falls. During 1910, at the beginning of which year the company commenced the manufacture of cyanamide, the exports of cyanamide to the United States were valued at \$211,200, while during 1911 these exports had increased to \$338,775. The exports for the current year are expected to be much greater, making the additional plant necessary to keep pace with the growing demand.

Alloys for Resisting Acid.

According to *The Engineer* it is reported that Professor Borchers, of Aix-la-Chapelle, a well-known metallurgist, has proved that it is possible to produce alloys of iron which will resist entirely the action of acids; while the materials used and the articles produced can be manipulated by the usual workshop methods. The new alloys are prepared by adding from 2 to 5 per cent of molybdenum to an alloy of ferrochrome which contains no carbon or very little. The alloy used must not contain less than 10 per cent of chrome. An alloy which contained only 36 per cent of iron against 60 per cent of chrome, and a very little molybdenum, was found to be insoluble even in boil-aqua-fortis, while it possessed all the solid qualities of iron and could be worked in the usual way. Not quite such favorable results were obtained by adding titanium and vanadium.

BOOK REVIEWS.

The Colloidal and Crystalloidal State of Matter. By Dr. Paul Rohland, translated by W. J. Britland and H. E. Potts. D. Van Nostrand Co., New York.

This is a descriptive pamphlet written for general orientation in the field of colloids.

The weighty position which substances in the colloidal state assume in numerous industries makes this

little book of special interest to the chemical technologist. Cement manufacture, concrete and porcelain manufacture, manufacture of pottery and enamelled ware, soap manufacture, beet sugar manufacture, dyeing, tanning, rubber, paper, the tungsten lamp, gold, ruby, glass, purple of Cassius, blasting gelatine, photography, bacteriology, all are concerned more or less with substances in the colloidal state.

As a general statement of the science of colloids to date, this pamphlet seems a very useful one.

Higher Mathematics for Chemical Students. By J. Riddick Partington. D. Van Nostrand Co., New York.

The introduction, well worthy of a text on chemical philosophy, "shows that the business of scientific investigation is the tracing out and classifying of the relations existing between phenomena. The first duty of mathematics in the service of physical science is to provide a method of expressing this relationship between phenomena."

The entire text is a study of the mathematical representation of the connection between phenomena.

Notes on Qualitative Analysis. By Beyers and Knight. D. Van Nostrand Co., New York.

The reviewer believes that no textbook of qualitative analysis was ever written that was entirely satisfactory to any teacher of the subject but the author himself. The reason for this lies chiefly in the fact that in no two institutions are the conditions, under which the course in qualitative analysis is given, the same.

The book under review, being designed to meet conditions in the laboratories of the authors and published by them chiefly for home consumption, probably meets those conditions, in an entirely satisfactory manner. It seems doubtful, however, that many other teachers of analytical chemistry will find the book suited to their needs.

A glance at the table of contents would indicate that not only are given the reactions and schemes for the separation and identification of the metallic and non-metallic radicals, and general discussion of the analysis of inorganic bodies, rare metals as well as common, but also a detailed account of the theory of electrolytic dissociation and its application to qualitative analysis. All this in the space of 160 not large pages. The theoretical material is complete as to subject matter but so brief in detail as to make it extremely difficult of logical comprehension by the student, unless he be already equipped with a fair knowledge of physical chemistry, a condition rarely met with in courses in qualitative analysis. The parts on theory and on the practice of analysis are entirely separate, no reference to the former being made in the course of the latter.

The general reactions and schemes for the separation of the metals are about as most brief texts of the subject give them. There is too little detail, both of instruction and of explanation, in connection with the systematic scheme of analysis.

The book is well printed on good paper, and is attractively and substantially bound.

A Text-book of Inorganic Chemistry. By G. Senter. D. Van Nostrand Co., New York.

A book of nearly 600 pages of rather small type, designed "for use in University, Technical Institutes and other general classes on the subject, and contains all that is usually included in a B. Sc. course." A "General Chemistry" not very different from a number of others. There is nothing striking about it, either of merit or the reverse.

In arrangement, the book is superior to many of the older texts designed for the same purpose in that considerable space is given to facts before any attempt is made to develop theory. The gases, oxygen, hydrogen and chlorine, and water, are discussed in detail, together with the general properties of gases, liquids and solutions. This occupies 100 pages and is followed by the development of the laws of chemical combination, the atomic and molecular theories, and the determination of the atomic weights. At this point formulation is introduced.

It seems to the reviewer that it would be better from the teaching standpoint to give less theory at this point leaving the molecular hypothesis and the determination of atomic weights until the student had acquired more chemical facts and become more accustomed to the use of hypothesis. The arrangement of the material on the theoretical foundations of the science is not always the best, but its expression, in general, is very simple and clear. The theory of electrolytic dissociation is discussed in connection with the general subject of electrolysis, but is not applied in the other parts of the book.

The study of the elements themselves is from the standpoint of the periodic classification. The descriptive matter is good, but rather more lengthy and detailed than necessary or advisable in an elementary college text.

Triumphs and Wonders of Modern Chemistry. By Geoffrey Martin. D. Van Nostrand Co., New York. Price \$2.00.

The author of this book states in his preface that "This book was written in order to awaken interest of the general reader and the young student in what is, after all a grand science. It represents an effort to give the general reader a picture of the world in which the chemist wanders and an idea of the great and wonderful problems with which modern chemistry deals."

The book states in a popular way many of the modern discoveries in chemistry and places the chemical theory in such a way that it can be understood by the general reader not particularly familiar with the science of chemistry.

It is particularly good in giving illustrations where the chemical theory is connected to common phenomena and common occurrences of everyday life.

This book is a good one to place in the hands of a young student to stimulate his interest in chemistry.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, Washington, D. C.

1,028,047. **Composition of Matter.** Joseph Russel Cornell Marsh, Cincinnati, Ohio, assignor to Marsh Steel Company, Cincinnati, Ohio, a corporation of Ohio. Patented May 28, 1912. This is a composition of matter for treating cast iron and steel which consists in a chemical mixture containing manganese, silicon, copper, chromium, boron, and arsenic.

1,028,070. **Process of Refining Iron or Steel.** Karl Albert Frederik Hiorth, Christiania, Norway. Patented May 28, 1912.

1,034,599. **Process of Manufacturing Alkali Hydroxids.** Arvid W. Ekstrom, Los Angeles, Cal. Patented August 6, 1912.

1,034,652. **Process of Preserving Timber** by Means of Phenolate Solutions. Friedrich Seidenschur, Charlottenburg, Germany. Patented August 6, 1912.

1,034,658. **Method of Bleaching.** Eduard Steiger, St. Gallen, Switzerland. Patented August 6, 1912.

1,034,677. **Baking-Powder.** David Beatty, Berkeley, Cal. Patented August 6, 1912.

1,034,680. **Artificial Timber.** Simon Bitterman, Clayton, New Mexico. Patented August 6, 1912.

This composition for building purposes, comprising coke breeze mixed with cement in the proportions of substantially 92% of the former and 8% of the latter.

1,034,784. **Method of Producing Refined Metals and Alloys.** Albert E. Greene, Pueblo, Colo., assignor to American Electric Smelting and Engineering Co., St. Louis, Mo., a corporation of Missouri. Patented August 6, 1912.

1,034,819. **Paint and Varnish Remover.** James Nickles, San Francisco, Cal., assignor of one-third to William G. Weiss, San Francisco, Cal. Patented August 6, 1912.

1,034,949. **Producing Metal Filaments.** William C. Arsem, Schenectady, N. Y., assignor to General Electric Company, a corporation of New York. Patented August 6, 1912.

The process consists in mixing refractory metal powder with ductile metal, and subsequently heating to fuse ductile metal, and subsequently heating to a higher temperature to vaporize the ductile metal and produce a coherent body of refractory metal.

1,034,974. **Method of Converting Ammonium Sulfite into Ammonium Sulfate.** Karl Burkheiser, Hamburg, Germany. Patented August 6, 1912.

1,035,120. **Process of Manufacturing Steel.** Henry D. Hibbard, Plainfield, New Jersey. Patented August 6, 1912.

1,035,280. **Manufacture of Steel.** William R. Walker, New York, N. Y. Patented August 13, 1912.

1,035,787. **Method of Making Pavements, Roads or Streets, and Cellar-Floors or the Like.** William T. Headley, Philadelphia, Pa., assignor to Headley Good Roads Company, Wilmington, Del., a corporation of Delaware. Patented August 13, 1912.

1,035,812. **Process of Extracting Alumina and Potash from Feldspar.** Samuel Peacock, Baltimore, Maryland, assignor to American Acid Company, Baltimore, Md., a corporation of Maine. Patented August 13, 1912.

1,035,829. **Art of Treating Starch and Starch Materials, and Product.** Alexander P. Anderson, Chicago, Ill. Patented August 20, 1912.

1,035,919. **Reduction of Boron Compounds.** Frank J. Tone, Niagara Falls, New York. Patented August 20, 1912.

1,035,960. **Treated Iron Ore.** Edward F. Goltra, St. Louis, Mo. Patented August 20, 1912.

1,035,972. **Process for the Removal of Carbon Disulfid from Gases.** Emil Knoevenagel, Heidelberg, Germany, assignor to Athion-Gesellschaft mit beschränkter Haftung, Mannheim-Waldhof, Germany, a society of Germany. Patented August 20, 1912.

1,036,121. **Method of Making Halogens.** Coulter W. Jones and Arthur E. Schaeffer, Midland, Michigan, assignors to The Dow Chemical Company, Midland, Mich., a corporation of Michigan. Patented August 20, 1912.

1,036,176. **Explosive Charge and Explosive Body for Projectiles, Mines and Torpedoes.** Christian Emil Bichel, Hamburg, Germany, assignor to E. I. du Pont de Nemours Powder Company, Wilmington, Del., a corporation of New Jersey. Patented August 20, 1912.

1,036,241. **Aromatic Ammonium Compounds and Process of Making Same.** Henry Stalay and Arthur Holt, Ludwigshafen-on-the-Rhine, and Otto Schmidt, Mannheim, Germany, assignors to Badische Anilin & Soda Fabrik, Ludwigshafen-on-the-Rhine, Germany, a corporation. Patented August 20, 1912.

1,036,267. **Print-Drier.** Ernest S. Krantz and John W. Knuteson, Minneapolis, Minn. Patented August 20, 1912.

1,036,306. **Distillation Process.** Stephens Neal, Cordele, Ga., assignor to The Neal Naval Stores Company, Cordele, Ga., a corporation of Georgia. Patented August 20, 1912.

1,036,362. **Method of Producing Carbon Black.** John A. Snee, West Elizabeth, Pa. Patented August 20, 1912.

This is a method of producing carbon black by introducing hydrocarbon gas into a highly heated zone and depositing within such zone the resulting carbon black on a surface of lower temperature than that portion of the zone in which the gas is decomposed.

1,036,405. **Art of Making Iron-Albuminous Compounds.** Fritz Zuckmayer, Elberfeld, Germany, assignor to Dr. Walther Wolff and Company, Gesellschaft, mit beschränkter Haftung, Elberfeld, Germany. Patented August 20, 1912.

1,036,434. **Compound for Hardening Steel and Other Metals.** Patrick Brennan, Philadelphia, and Michael Meehan, Williamstown, Pa. Patented August 20, 1912.

1,036,453. **Process of Producing Aluminum Fluorid.** David H. Childs, Alfred, New York. Patented August 20, 1912.

1,036,461. **Process of Making Fire-Extinguishing Compound.** Edward M. Davidson, New York, N. Y., assignor to Pyrene Manufacturing Company, a corporation of Delaware. Patented August 20, 1912.

1,036,498. **Process of Making Steel.** Fred R. Lamb, Bettendorf, Iowa, assignor of one-fourth to Albert R. Frier, Davenport, Iowa. Patented August 20, 1912.

1,036,506. **Hydraulic-Cement and Water Paint.** William P. D. Moross, Chattanooga, Tenn. Patented August 20, 1912.

1,036,576. **Attaching Rubber to Metals.** Leo Daft, Rutherford, New Jersey, assignor to Electro-Chemical Rubber & Manufacturing Co., a corporation of New Jersey. Patented August 27, 1912.

The method consists in making a solution of a plurality of metals, to one of which rubber may be chemically united, electro-plating the article to which it is desired

to attach the rubber in such solution, obtaining a deposit containing such metal and attaching the rubber to the surface thus formed by vulcanization.

- 1,036,611. Process of Manufacture of **Alkaline and Earthy-Alkaline Nitrates**. Philippe Auguste Guye and Georges Darier, Geneva, Switzerland, and Allart van Volten, Haarlem, Netherlands. Patented August 27, 1912.
- 1,036,622. Process for Producing **Thyroid-Gland Extracts**. Ernst Hoennicke, Dresden, Germany. Patented August 27, 1912.
- 1,036,705. Method for the Production of **Anhydrous Hydrosulfites**. Emil von Portheim, Prague, Austria-Hungary. Patented August 27, 1912.
- 1,036,706. **Wood Preserving Compound**. Edwin L. Powell, New Orleans, La. Patented August 27, 1912.
- 1,036,712. Process of Producing Cementitious Products. Samuel W. Ramsey, Kent, Ohio. Patented August 27, 1912.
- 1,036,715. Process for **Condensing Glycerin**. William Rintoul and Alfred George Innes, Stevenston, Scotland, assignors to E. I. du Pont de Nemours Powder Co., Wilmington, Delaware, a corporation of New Jersey. Patented August 27, 1912.
- 1,036,880. Production of **Alizarin**. Carl Mollenhoff, Leverkusen, near Cologne, Germany, assignor to Farbenfabriken vorm. Friedr. Bayer & Co., Elberfeld, Germany, a corporation of Germany. Patented August 27, 1912.
- 1,036,897. Process for Extracting **Alumina** from Feldspar. Samuel Peacock, Chicago, Ill. Patented August 27, 1912.
- The process consists in producing an alkaline aluminate containing potash from feldspar; treating the aluminate with carbon dioxide to separate out a portion of the potash; and then digesting the aluminate with amorphous silica to remove the remainder of the potash.
- 1,036,898. Method of Rendering **Cement Mortar and Concrete Waterproof**. Roy Alfred Plumb, Detroit, Mich., assignor to Trussed Concrete Steel Company, Detroit, Michigan, a corporation of Michigan. Patented August 27, 1912.
- 1,036,906. **Granular Explosive**, Especially Suitable for the Preparation of Pressed Pieces and Method of Making the Same. Otto Reiter, Schlebusch-Manfort, Germany, assignor to E. I. du Pont de Nemours Powder Company, Wilmington, Del., a corporation of New Jersey. Patented August 27, 1912.
- 1,036,909. Process of Making **Fertilizers**. Ludwig Saarbach, New York, N. Y. Patented August 27, 1912.
- 1,036,958. **Tanning Compound**. Daniel W. Brown, Colesburg, Tenn. Patented August 27, 1912.
- 1,036,946. Composition for **Removing Paint or Varnish**. John M. Wilson, Montclair, New Jersey, assignor to Wilson Remover Company, Newark, New Jersey, a corporation of New Jersey. Patented August 27, 1912.
- 1,036,995. Process for Hardening **Steel Castings**. John W. Gebhard, Muncie, Indiana, assignor to Armor Steel & Foundry Co., Chicago, Ill., a corporation of Arizona. Patented August 27, 1912.

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PROGRESS IN INDUSTRIAL CHEMISTRY.*

By RUDOLPH MESSEL.

At a time when the latest discovery of interest may be instantly flashed to the remotest part of the world by wireless telegraphy, and the technical press discusses every possible problem as it arises, a presidential address seems to me to be almost an anachronism. In very few cases is it possible to communicate anything not already known. Whatever issue a speaker may desire to consider is sure to have been dealt with till it is almost threadbare, and I fear that the topics I venture to bring before you must be enrolled in the latter category.

I propose to deal with some aspects of the remarkable progress made within my recollection. The ceaseless energy with which industry has availed itself of the achievements of pure science has made possible the manufacture, on a large scale, of products either unknown but a few years ago, or seen as specimens in scientific collections, or produced only by nature. That I shall refer to relatively very few of these triumphs of chemical research and invention and mainly to inorganic products must be evident when I mention that the period covered embraces the discovery of the aniline dyes and that of artificial rubber, as well as the invention of the first electric telephone and of wireless telegraphy.

As my recollections unfortunately go back over so long a period, I feel tempted to drag in here one which may be of interest to some of my audience, though it has no connection with the matter I propose to deal with. In 1861, when I was at school at Friedrichsdorf, in Germany, my master, Philip Reis, invented the first telephone. I was present at its birth and assisted Reis in making the mechanical parts of some of his instruments and also repeatedly in his experiments, Reis being at one end of the circuit speaking or singing, I listening at the other, or *vice versa*.

The introduction of synthetic processes may be said to be the keynote of progress of modern industrial chemistry.

One of the most fascinating compounds recently introduced into industry is *calcium carbide*, CaC_2 . It

had lain dormant since its discovery in 1862 by Wöhler until your countryman, Wilson, and Moissan made use of the electric furnace to produce it; now its manufacture constitutes a mighty industry, close on 300,000 tons being produced annually. Serving as it does as raw material for the manufacture of calcium cyanamide, it is now the parent of numerous other products of great importance. Among these may be mentioned *acetylene*, C_2H_2 , so largely used as an illuminant, and for welding and cutting metals, and I may remind you that the possibility is foreshadowed that this gas will be of use as the starting point in making other chemicals. *Calcium cyanamide*, apart from its undoubted great value as a fertilizer, is coming to the fore as a source of *cyanides*, now so largely used in extracting gold. What may be of far greater importance, it is convertible by the action of superheated water into *ammonia*, which in turn may be converted into *nitric acid* and nitrate of ammonia by oxidation with air under the catalytic influence of platinum.

I have recently noticed alarming reports in the press, that the impossibility of procuring supplies of nitrate of soda from Chili in time of war may prove a serious handicap to any country in the production of explosives and powder. Considering that the quantity of nitrate of soda used for the purpose is but a fraction of that required in agriculture and that large stocks are held for this purpose almost everywhere, I cannot share the writer's fear. But in view of the fact that ammonia salts are produced by all gas works and of the many attempts to produce it synthetically, the catalytic method of producing nitric acid from ammonia may deserve more attention than it has received up to now, especially if ammonia, no matter how produced, should become a sufficiently cheap raw material.

The most interesting feature in the production of calcium is the use of pure nitrogen. Of the various methods of preparing the gas, that which involves fractional distillation of liquefied air seems to be preferred. We are becoming familiar in industry with the impossible, but who *could have expected* such a possibility only a few short years ago? Think of the excitement caused in the scientific world when, in 1877, Pictet and Cailletet first succeeded in liquefying oxygen. Pictet's work was then described as the most

*Address delivered by the President of the Society of Chemical Industry at the Chemists' Club, New York, September 3, 1912.

brilliant achievement in modern science. The barrier between condensable and permanent gases was broken down and the latter term was deprived of its significance; but how much work remained to be done, what ingenuity had yet to be exercised, to translate this scientific discovery into a process for the industrial preparation of nitrogen! Success has been achieved by the exertions and ingenuity of several of our greatest authorities in physical and chemical science; nowadays every gas that is required is readily procurable in the liquefied form (Cl_2 , SO_2 , N_2O , CO_2 , NH_3 , etc., etc.) in the well-known steel cylinders capable of withstanding enormous pressures.

If I have laid stress on the conversion of ammonia into nitric acid, the reason is that ammonia is obtainable locally everywhere, either as a by-product of the manufacture of illuminating gas or Mond gas and from coke ovens, and that the installation for converting it into the acid is a relatively cheap one. The numerous attempts to produce ammonia synthetically from its elements nitrogen and hydrogen, or from various *nitrides*, such as those of titanium, boron, magnesium, aluminum and calcium, can moreover only be of benefit in solving the problem. True, the direct production of *nitric acid* by means of the *electric arc* from atmospheric air may appear to be a more rational process, but so long as this industry is tied to water power, and the difficulties of transporting nitric acid as such in aluminum or iron packages be not overcome, the case seems different in my judgment, particularly in countries where water power is not available and other power is yet too expensive. It is to be remembered that to carry nitric acid safely in iron packages about 10 per cent of concentrated sulphuric acid has to be added, and that if one or the other of the ammonia processes under trial should make it possible to transport it as nitrate of ammonia, from which it can readily be liberated at the place of consumption, the difficulty of carriage in the event of war would still remain.

My reason for referring at such length to the production of these compounds of nitrogen is their importance in agriculture. Food the nations must have, and it seems that to this end they will require the services of the chemist more and more as population grows. The great stimulus our medalist, Sir William Crookes, has given to the production of nitric acid by calling attention to the near approach of the exhaustion of the deposits of nitrate of soda is well known. His suggestion to utilize Cavendish's discovery of the direct interaction of the constituents of the atmospheric air and the success so far achieved have often been referred to; the work done by Birkeland and Eyde, by Schoenherr, Pauling and others is also well known, but it gives me particular pleasure to point out that here again America was the first to attempt the realization of this great problem. The realization of the other great problem—*i. e.*, the production of *ammonia from its elements*—appears likewise on the eve of ac-

complishment, and I hope it will not be long before we shall have details of the manner in which it has been solved in practice, and how the great technical difficulties have been overcome. It will likewise be interesting to learn something about the relative efficiency of the various uranium and iron catalytics used, etc. If the published particulars as to temperature (about 650°) and pressure (about 150 atmospheres) be correct, the task to be solved was one of no mean order. Meanwhile we can only offer our best wishes to the ever-enterprising Badische Anilin- und Soda Fabrik.

Two of the other processes mentioned before, namely, that of the production of ammonia from *calcium nitride* and from *aluminum nitride*, are likewise most interesting, the former for chemical reasons—*i. e.*, the conversion of metallic calcium first into calcium nitride, Ca_3N_2 , then by the action of hydrogen on this compound into *calcium hydride* and ammonia, the calcium hydride being subsequently reconverted by means of nitrogen into calcium nitride and ammonia—so that a relatively small quantity of *calcium* is theoretically sufficient to produce an infinite quantity of ammonia. Numerous processes have been devised for producing *hydrogen*; one of the latest is Pictet's, who splits up hydrocarbons either directly into hydrogen and carbon or by means of steam, at the melting point of iron, into hydrogen and carbon monoxide, thus materially increasing the yield.

Inasmuch as *aluminum nitride* yields on hydrolysis, together with ammonia, a particularly pure form of *aluminum* hydrate, starting from an impure raw material, it may become of great importance to the aluminum industry. I well remember aluminum and more often magnesium being made by Bunsen by the electric arc on a diminutive scale as a lecture experiment. We students used to cough violently when the white fumes which were given off began to fill the lecture room until Bunsen, smiling pleasantly, mentioned that the white fumes were due to the ammonium chloride he had added to keep the surface of the metal bright and that ammonium chloride was an excellent remedy for a cough. The coughing then stopped. As a curiosity, bars of the metal about 3 ins. by 1 in. by $\frac{1}{2}$ in. were handed round and weighed by everyone in his hand; the metal was doubtless produced by St. Claire Deville's sodium process. The annual output of aluminum in 1909 was over 24,000 tons, produced electrically. Now that the problem of autogenous welding of the metal, which so long defied all efforts, has been solved, the use of aluminum for chemical apparatus has become practical; apart from its utility in handling nitric acid, the metal has proved to be of the greatest value in breweries, in the food industry and varnish works.

The application of aluminum as a fuel by Goldschmidt has further led to the production, by his Alumino-Thermite process, of many metals in a relatively pure form otherwise only producible by the

agency of the electric current. Chromium, manganese and molybdenum prepared by this method, besides various alloys of nickel, iron and copper with these metals, or with titanium and vanadium, have found a use mainly in the iron industry. The igneous process of welding rails and repairing castings by means of the Thermite process is of course known to all, as well as the use of tungsten and tantalum as filaments in electric incandescent lamps. The fact that tantalum filaments, of vastly greater strength than those formerly produced by compression of the metal in powder form, can now be obtained by drawing the metal through diamond dies will doubtless give an increased stimulus to the use of the element. The mention of tantalum may call to your mind the fact that the expression rare is fallen into disuse, as the earths once known as rare are in everyday use, and, owing to the scientific acumen displayed by Auer von Welsbach, the gas industry is now well able to hold its own against the electrical. But electricity is in evidences everywhere in our industry. It threatens to displace the furnace in the alkali works, it provides us with chlorine, and the time may not be distant when muriatic acid is made electrically. We are indebted to the electric furnace for the sodium industry (with its application to the cyanide, sodium amide and other manufactures) and to the production of ferrosilicon, carborundum and graphite, for which, in the form of electrodes and lubricants, America, thanks to Mr. Acheson, remains as yet unsurpassed. The manufacture of nickel by the remarkable Mond carbonyl process should not be forgotten. This metal would appear to have some future in the elimination of carbon bisulphide from coal gas and possibly as a catalytic in other industries. We do not, however, always want to get rid of sulphur. A most original idea, successfully carried into practice by Frasch in Louisiana, is no doubt that of liquefying sulphur in the bowels of the earth and then pumping it up.

After thus rambling through the highways and byways of inorganic chemistry, we now arrive at a different class of industries. There is no need to go into any detail, but suffice it to say that their influence has been of momentous importance industrially, and in turn has acted and reacted greatly on science. Merely to mention them is sufficient. I refer, of course, to dyestuffs and synthetic organic products, including drugs. I will not weary you by repeating what has been related so often and so fully. It is, however, noteworthy that from the outset the establishment of new industries, based on the discovery of aniline dyes and of methods of producing alizarin and indigo artificially, has in turn given rise to many others, as the organic and inorganic chemicals they required, which were little, if at all, known to commerce at the time, had to be produced on a large scale. Benzol, nitrobenzol, aniline, to mention only a few, were among the newcomers; later on came anthracene.

The coal tar industry is now the largest consumer

of inorganic products and was the cause of the invention of the catalytic process of manufacturing sulphuric anhydride. May I be allowed to relate how I came to be connected with this industry? I was a pupil of Professor Strecker at Tübingen in the later sixties. When subsequently, in 187—, I again met him and his brother—who was a chemist at Hoechst—and Dr. Brüning, one of his pupils, he spoke of the importance of fuming sulphuric acid in the alizarin industry. The process of sulphonating anthraquinone had been introduced or was about to replace Perkin's dichloranthracene process, the use of ordinary concentrated oil of vitriol having proved to be very destructive to the anthraquinone at the elevated temperature that had to be employed. To my question how this fuming acid could best be made, he replied, "That is a problem for you to solve." A few experiments convinced me that, given pure gases, the catalytic action of platinum was the rational solution of the problem; I had to wait, however, for an opportunity of carrying my idea into practice. This came when, in April, 1875, a telegram reached me from my then principal, Mr. W. S. Squire, asking me to read up that night about Nordhausen acid as it was required by an alizarin works. I showed Squire how simple a matter it was to bring about the combination of sulphur dioxide and oxygen by means of platinum and other catalytics, but it was not until at his request I had carried out a number of experiments with bisulphates, etc., which were not very successful, that he asked me "to try my dodge;" henceforward we worked conjointly on the production of the anhydride by catalytic action. Though the process was patented in Squire's name, Sept., 1875, as others were afterwards or in the name of Neal, they are the joint work of Squire and myself. Soon after, in the 2nd October Heft of *Dingler's Polytechnisches Journal*, Winkler published an account of his process, which was practically identical with ours. Both of us erred at that time in believing that stoichiometrical proportions of the gases were best to use, and the various similarities gave rise to unpleasant comment. In letters, however, which I possess, Winkler freely acknowledges the independence of our work and only regrets that he had deprived himself of the benefit of the invention of his publication, but he was anxious to work with us.

I cannot leave this chapter without paying my tribute to the work done by others in developing the catalytic process, and foremost, to the late Dr. Kneitsch and his co-workers in the Badische Anilin- und Soda Fabrik. At the same time I will let you into one or two secrets. The one is that so far I have not been successful in working with the spent oxide of gas works. It has the advantage of relative freedom from arsenic, but the drawback of producing an acid which is not so bright and colorless as that made from pyrites. The color is due to the organic matter in the raw material and to the formation of nitric oxide from its nitrogenous constituents. Nitric oxide can be traced

in the burner gases and it is not eliminated in the washing process to which the gases are submitted. Another point is that there is a loss of platinum amounting to about 1 grain per ton of monohydrated acid produced; the loss must be of a mechanical nature and can be detected in the drips, although actinium is not discoverable in the gases at this enormous dilution. I believe I can find confirmation of the assumption that the platinum is carried forward owing to the rapidity of the current, because in none of the processes I have worked at a relatively low velocity have I found any loss of platinum, except such as is unavoidable in extracting the asbestos.

Fuming sulphuric acid has found its chief use in the coal tar color industry, in refining certain petroleum oils—mainly the Russian oils—and vaseline, and in the explosive industry. As nitrocotton forms the basis of the celluloid industry, which has been so greatly developed of late, I must mention it and the rivals which it has found in acetyl and cuprammonium cellulose, and last, but not least, in the viscose discovered by Cross and Bevan. These materials are used in large quantities for the production of artificial silk, photographic films and artificial hair; nor must I omit to mention the important wood pulp industries depending on chemical processes.

Sufficient examples have been given to illustrate my case: to show that science and industry are working hand in hand, and the importance of the result which such co-operation has produced.

In fact, no branch of industry has been left untouched by the ceaseless and irresistible advance of chemical science and technology.

And now when we look back on this long list of chemical industries which I have brought before you and their great variety, we have to ask ourselves: Can a chemist be so trained that on entering into any kind of works he will at once be of use and efficient, apart from the expectation that, as a matter of fact, he is supposed to be a proficient analyst? My answer is in the affirmative, provided that the employer himself knows something about the industry in which he is engaged; in that case, he will be patient and not expect too much from a beginner.

My illustrations must serve to show that if the student is but to know the chemical and physical principles which underlie so wide a range of activity as any one of the industries I have pictured provides, his time will be more than occupied; to expect him to be conversant also with the technical and economical aspect of industrial problems and to be able to apply his knowledge forthwith is going too far. Technical training can be of real value only after a sound foundation in the principles and practice of pure science has been acquired. Again do I ask: Can such technical knowledge be acquired by the student before entering into practice as well as the scientific knowledge that will be of use to him and his employers in all or the majority of the industries I have enumerated? It

is evident it cannot; and if it cannot be done, is it worth the student's while to sacrifice much time at the most important and critical part in his life, as far as learning is concerned, in acquiring technical knowledge which may be of no assistance to him in after life.

Too early concentration on special subjects must have a bad effect on the development of the power and habit of thinking independently and on the development of the faculty of imagination in the student. If he can find time, apart from his bread and butter education, it is much better for him to turn his mind to subjects of general culture, such as history, art and literature. Experience teaches me that technique is very readily acquired in practice by one who has been scientifically trained. The most important task of the employer in industry, as in every other walk in life, is to find the right man; and the right man with scientific knowledge, who has imagination and power of observation and can select and command competent subordinates, is immeasurably more useful than the otherwise right man without scientific knowledge. Before all things, it is necessary to find the right man; experience and inventive faculty must do the rest. It is not that we do not possess sufficient knowledge when we leave our college as students; what we lack is experience and the power of applying our knowledge. Our great chemical industries have been originated and developed by scientifically trained men; to name only a few, men such as Perkin, Caro, Brunck, Solvay and Mond, YOUN, the Siemens's, Duisburg, have never found any difficulty in securing the co-operation of engineers or electricians competent to construct any kind of plant they have required to carry out their problems.

In fine, Carlyle has well said: "He who has learned how to learn can learn anything;" the best system of education is the system which teaches each man how to educate himself.

Our education really begins when we leave college and the storm of life forms our character. We have to study, as nothing in this world is given to us for nothing; books, our scientific and technical societies, must assist us.

Had time permitted, much might have been said of industries which are almost specifically American and of developments that are now taking place in connection with the manufacture of food supplies. My difficulty has been merely to indicate the vast number of directions in which the chemist is now rendering service to society. Each one of my hearers will be able to enlarge upon one or the other of the topics to which I have referred. I can ask you now only to reflect how much lies behind my story. The progress witnessed in my time is inconceivable. It is impossible for one of my position to do justice to such a theme, but of its infinite importance to our civilization there can be no question.

SYNTHETIC AMMONIA.*

By H. A. BERNTHSEN.

You all know that of the chemical elements that occur in large quantity on our planet, nitrogen is one which is characterized by its complete indifference to chemical attack. Berzelius already says of it: "It is difficult to recognize because it does not differ from other gases by any conspicuous property, but can only be recognized by means of properties which it does not possess." We see therefore both in science and in arts that nitrogen is frequently used when it is desired to protect bodies from chemical attack by oxygen or when the commencement of an oxidation is to be prevented. The vacuum of the thermometers in instruments which are intended for high temperatures is, as you are aware, filled with nitrogen. The storage of readily combustible liquids, such as coal-tar benzene and light petroleum naphtha, is effected by covering these bodies with nitrogen; their transport by applying compressed nitrogen. It is to the indifference of this element to chemical attack that the curious state of affairs must be attributed, that although we are dependent for all the conditions of life on compounds of this body and although we live in an infinite ocean of nitrogen, yet up to a short time ago we were not in a position to obtain nitrogen compounds from it. We were forced to cover our requirements of saltpeter for gunpowder, of nitric acid for gun-cotton and for nitration and many other applications, of ammonia for refrigerators, for instance, and so on, not by drawing upon the nitrogen of the air, but by utilizing ready formed nitrogen compounds, which ultimately result from the processes of plant life of earlier times. On the one hand Chili saltpeter and on the other hand the ammonia liquor obtained in small proportions as a by-product in the manufacture of gas or coke from coal served to supply the wants mentioned. We were also and in particular dependent on these two sources of nitrogen for the requirements of agriculture, which are far greater than all the other taken together.

But now, while the requirements of nitrogenous manures are constantly increasing, in order to guarantee to the inhabitants of the world sufficient harvests, we have in all probability to reckon with a comparatively rapid diminution of the supply of natural Chili saltpeter. On the other hand we cannot expect the balance to be maintained by a rapid increase in the production of ammonium sulphate, for this is dependent on the manufacture of gas and of coke, which increases but slowly. To this, some working up of peat may be added, but a production of ammonia in this way as the main object of manufacture is impossible. The problem of the conquest of elementary nitrogen, of forcing this obstinate scamp into the service of our civilization, has consequently attained immediate im-

portance for some time. Already three years ago at the Seventh International Congress of Applied Chemistry in London, I therefore had the honor of reporting on the utilization of atmospheric nitrogen and a new way for the production of nitrates from the air.

It might appear that the American continent, which is so richly blessed with the treasures of nature, can perhaps await with greater patience the development of events than could most European countries. For while the soil of the latter has been worked to the uttermost through centuries of agriculture, the unexampled development of this country has been caused, to a great extent, by the fact that agriculture had virgin soil at its disposal wherever it developed. There may still be places, such as the English poet Browning sings of:

Nature frames

Some happy lands, that have luxurious names,
For loose fertility; a footfall there
Suffices to upturn to the warm air
Half-germinating spices; mere decay
Produces richer life; and day by day
New pollen on the lily petal grows,
And still more labyrinthine buds the rose.

In general, however, a change is occurring. The soil of the eastern states, if it is to yield full harvests, in the future already requires the addition of manures above all of the nitrogenous manures, for lack of the latter is most quickly noticed by the plants. A similar treatment would further be of great advantage in many parts of the southern cotton states. Finally, in the course of years, the same requirements will be noticed in the west more and more, as the development of hitherto uncultivated land even there hardly comes any more into consideration. Nature will only continue to shower her favors on man if he adapts himself with reason to her immutable laws, as expressed by the poet:

Nur der verdient sich Freiheit wie das Leben,
Der täglich sie erobern muss.

I therefore count upon your interest if I deal today in some detail with the nitrogen question, and announce to you some of the progress that has been made since the last Congress.

The three methods employed for the fixation of nitrogen are: *first*, the direct oxidation of nitrogen of the air forming nitric acid, nitrates, etc.; *second*, the synthesis of ammonia from nitrogen and hydrogen; and *third*, the fixation of nitrogen to metals or metaloids and, if desired, subsequently decomposing the resulting products, nitrids, etc., producing ammonia. Three years ago it was the first of these ways with which I dealt principally. I was in a position to announce that in the processes of Birkeland of Christiania, on the one hand, and of Schönherr and the Badische Anilin & Soda-Fabrik, on the other hand, two important ways had been opened up for oxidizing the atmospheric nitrogen with the aid of electricity obtained from water-power. Two companies had been formed by a Norwegian-French group, the Norsk Hydro Elektrisk Kvaelfstofaktieselskab, and a German group, the Badische Anilin & Soda-Fabrik together

*Lecture by Herr Heilmrat Prof. Dr. Heinrich August Bernthsen, Managing Director of the Badische Co., Ludwigshafen-on-Rhine, Germany, Eighth International Congress of Applied Chemistry, New York, September, 1912.

with the Farbenfabriken of Elberfeld and the Actien-gesellschaft für Anilinfabrikation of Berlin. These undertakings and some other associated enterprises have in the meantime been developed with great energy and the factory at Saaheim, which converts about 120,000 H. P. of the Rjukan fall into oxids of nitrogen, is now in full swing. The management of these works has passed into the hands of the Norwegian-French group by an arrangement with the German group.

The processes for the combination of nitrogen with metals, etc., producing metallic nitrids, cyanamids, and the like, and from these ammonia, have also progressed.

On the one hand the nitrolim obtained for instance by the union of nitrogen with calcium carbid, which is produced in several factories, is in part utilized directly as manure; in part a beginning has been made with the manufacture of ammonia from it by treatment with steam. On the other hand the nitrids, and especially those of aluminum and silicon, have been more closely studied. The process of Serpek for the production of aluminum nitrid has been developed by the Société Générale des Nitrures on a manufacturing scale in order to obtain on the one hand, pure alumina for the production of aluminum, and on the other, ammonia. Then again the Badische Anilin & Soda-Fabrik in following up its work on barium cyanid from nitrogen, barytes and carbon took up the study of the production of titanium-nitrogen compounds and that of silicon nitrid from silica, nitrogen and carbon, and then in connection with this the production of mixed nitrids of silicon and aluminum, and of aluminum nitrid itself. In this field of work also an arrangement has been made between the firms working it, the Badische Anilin & Soda-Fabrik having assigned their patents to the Société Générale, retaining for themselves certain rights of preparing the nitrids in question according to the patents of both companies. It is to be expected that this branch of industry will also develop satisfactorily.

I refrain from discussing any of these methods of fixing nitrogen and refer to the communications made by the inventors themselves and in particular to the lecture delivered a few days ago at this Congress, by Dr. Eyde, the general director of the Norwegian companies referred to.

I propose to deal today, however, from my own direct experience, with the development of the problem for the synthetical manufacture of ammonia from its elements. A few years ago the solution of this problem appeared to be absolutely impossible. It has recently been the object of very painstaking investigations by Professor Haber and the chemists of the Badische Anilin & Soda-Fabrik, and numerous patents have been taken out with reference to the manufacture. Apart from what is already published in this way, however, we have refrained from any other announcements until we were in a position to report something final with reference to the solution of the technical question.

This moment has now arrived and I am in the agreeable position of being able to inform you that the said problem has now been solved fully on a manufacturing scale, and that the walls of our first factory for synthetic ammonia are already rising above the ground at Oppau, near Ludwigshafen-on-Rhine; this factory will be opened by the middle of next year.

Permit me therefore to explain to you the fundamental points upon which this latest achievement of chemical industry is based.

The affinity of nitrogen for hydrogen, as is well known, is so small that the two do not appreciably unite with one another either at ordinary or at a raised temperature. It has long been known that by electric sparks or by a silent discharge very minute quantities of ammonia can be formed from nitrogen and hydrogen. Also by conducting a mixture of hydrogen with nitrogen prepared in a particular way over spongy platinum, Johnson (1881) thought that he had obtained ammonia, in a quantity amounting to 0.0059 of NH_3 per hour. The nitrogen had been obtained from ammonium nitrite and passed through ferrous sulphate solution in order to remove nitric oxids. But nitrogen prepared in other ways did not yield the ammonia, so that Johnson assumed that there were two modifications of nitrogen. Wright (1881) proved that ferrous sulphate did not absorb all the nitrogen oxids and that the ammonia was produced by the action of hydrogen on nitrogen oxid in the presence of platinum. When using pure nitrogen he also obtained no ammonia. Baker (1883) also came to the conclusion that Johnson's statements as to the production of ammonia from its elements were mistaken. In no case could Baker notice any signs of the formation of ammonia, and he decided that hydrogen does not combine with nitrogen under the influence of heated platinum sponge.

Ramsay and Young on the other hand (1884) determined the decomposition of ammonia by heat at various temperatures. In this research, among other experiments, a mixture of dry nitrogen and hydrogen was passed through a red-hot glass tube filled with iron filings, or through an iron tube. The presence of ammonia could again not be proved. When using moist gases they noticed the presence of traces of ammonia, the formation of which they explained by the decomposition of water and the production of nascent hydrogen.

Again Perman, twenty years later, occupied himself with the question of the formation of ammonia from its elements. Upon slowly passing a mixture of nitrogen and hydrogen (1 vol.: 3 vol.) through a glass tube heated to red heat, he obtained no ammonia, and the same result was attained when the tube was filled with porcelain. But when the mixture, in a moist condition, was passed over red-hot iron or several other metals, or over asbestos, pumice, pipe-clay, etc., traces of ammonia were formed, according to Perman's statement.

The investigations entered upon a new phase when

Haber, armed with the weapons of modern physical-chemical methods, attacked the problem of the estimation of the ammonia equilibrium in 1904 in conjunction with van Oordt. These investigators showed that at a temperature of about 1000°C . decomposition of ammonia into its elements was almost, but not quite, quantitative (of 1000 molecules of ammonia 999.76 were decomposed at a temperature of 1020°C .), and that consequently from these elements and under the same conditions very small quantities of ammonia were formed. The authors used as contact material, iron prepared from iron oxalate by heating to red heat in a current of hydrogen, and the iron was spread out upon purified asbestos. Further, for some experiments nickel was precipitated from nickel nitrate upon pure silica. From a mixture of nitrogen and hydrogen corresponding to 100 parts of ammonia they obtained at the temperature mentioned about 0.02 parts of ammonia, and even this figure was subsequently, by more accurate examination, shown to be still too high. In a further publication in 1905,² these results were confirmed and summarized in the following statement: at the temperature of commencing red heat and upwards, no catalyzer is capable of producing more than traces of ammonia. The work was carried out at ordinary atmospheric pressure "for practical reasons," and it was pointed out that even under considerably increased pressure the position of the equilibrium would remain very unfavorable. Manganese was also taken into consideration as a catalyzer, but its effect, as also that of nickel, was less satisfactory than that of iron.

While Haber in company with Le Rossignol³ pursued this line of research, Nernst communicated the results of similar investigations to the general meeting of the German Bunsen Gesellschaft at Hamburg in 1907.⁴ He was induced to take the matter up by the fact that Haber's figures showed a remarkable discrepancy from the equilibrium figures calculated according to the famous "heat theorem" of Nernst himself. In order to determine the otherwise so minute quantities of ammonia, Nernst worked under pressure, using as a rule about 50 and up to 75 atmospheres, for according to the well-known laws the concentration of the ammonia increases with the pressure. These results were published more in detail a year later by his co-worker, Jost.⁵ The latter used as catalysts besides platinum foil or iron (prepared from iron oxid in a current of hydrogen), also manganese (obtained from an electrically prepared amalgam by driving off the mercury in a current of ammonia). The figures here obtained for the equilibrium were still lower than Haber's, a fact which Nernst said was very regrettable, for otherwise one might really have thought of preparing ammonia synthetically from hydrogen and nitrogen. Haber and Le Rossignol made a further publication in 1908,⁶ having now made their

measurements also at a pressure of 30 atmospheres. By this means, it is true, the differences as against Nernst's experiments on account of the position of equilibrium, as also the maximum percentage of ammonia obtainable at a given temperature, were not quite got over, but at all events the figures of both scientists agreed in showing that this maximum is extremely low. At a temperature of 1000°C . the volume percentage of ammonia calculated for atmospheric pressure is 0.0048 per cent according to Haber and 0.0032 per cent according to Jost, the corresponding figures at 700°C . being 0.0221 per cent and 0.0174 per cent.⁷ That is, at these temperatures the ammonia equilibrium is extremely unfavorable, while at lower temperatures the catalytic action of the metals in question was too low to be able to work with them.

To sum up all these investigations on the direct combination of nitrogen and ammonia, it can be said that the problem seemed now to have become more than ever a mere dream, of which the realization appeared to be quite beyond the bounds of possibility, so that there was every reason why the scientist should turn his back on so unfruitful a field.

In spite of this, Haber had a feeling that a technical synthesis of ammonia from its elements could be rendered possible, and placed himself in communication with the Badische Anilin- & Soda-Fabrik for the promotion of the work. He then showed, still in 1908,⁸ that the technical preparation of ammonia from its elements can in fact be carried out, in spite of the unfavorable equilibrium and the low catalytic capacity of the contact metals used, if the mixture of nitrogen and hydrogen is kept under constant pressure during the whole of the operation and is subjected alternately to the catalytic formation of ammonia at a high temperature and then free from ammonia by absorption or condensation at a lower temperature. Care must at the same time be taken that the heat of the reaction gases containing ammonia is transferred afresh to the gas mixture about to be acted on. In other words, the nitrogen-hydrogen mixture circulates under continuous pressure, through the vessel for the formation of the ammonia, the vessel for the separation of the ammonia and a circulating pump, all these being connected up to a closed endless circuit. Of course it is advisable at the same time to replace with a fresh nitrogen-hydrogen mixture as much of the gas as is converted into ammonia.

It was further found when working according to this continuous process of Haber's under conditions which induce a relatively high concentration of ammonia that the advantages of heat regeneration are no longer of such vital importance, but that it is sufficient in this case to work continuously under pressure without the same time regenerating heat.⁹ Finally it was seen¹⁰ that it is not even absolutely necessary to work continuously under pressure (that is, to circulate the gases continuously under pressure) if the reaction

¹Z. anorg. Chem., 43, 111.

²Ibid., 44, 341.

³Ber., 40, 11, 2144 (1907).

⁴Zelt. für Elektrochemie, 13, 521 (1907).

⁵Z. anorg. Chem., 57, 414.

⁶Zelt. für Elektrochemie, 14, 181 (1908).

⁷Z. anorg. Chem., 57, 193; Zelt. für Elektrochemie, 14, 193.

⁸German Patent No. 237,421, October 13, 1908.

is carried out under very high pressure, for instance at about one hundred atmospheres, preferably, however, at from 150 to 250 atmospheres, and even higher. A range of pressure is hereby introduced which had never been touched in the synthesis of ammonia and was also something quite new in any manufacture, for no one had previously so much as thought of carrying out technically a catalytic reaction with gas currents at the necessary high temperatures under such an enormous pressure.

By these means, under a pressure of 200 atmospheres, at a temperature of from 650-700° C. and using an iron catalyst prepared from the purest iron oxid, occupying a space of 20 cc., and with a gas speed of 250 liters per hour (measured at ordinary pressure) it is an easy matter to obtain, for example, 5 grams, or per liter of contact space, 250 grams of ammonia in an hour.

The following further point comes here into consideration: All previous publications had in view exclusively the determination of the ammonia equilibrium, which can be found theoretically most accurately in a steady volume of gas. If a current of gas is used, the rate of flow must naturally be kept low, so that one may be sure that equilibrium is reached. Now there were no indications as to how far the concentration of the gas would be reduced when the rate of flow is raised, and whether the concentration would be sufficient when such a rate of flow is taken as must be done when working on a technical scale. Haber has therefore rendered signal service in showing that one can work successfully with such higher rates of flow.

A diagrammatic exposition of an apparatus used by Haber is shown on the chart¹¹ before you. The catalyst is in a metal tube which opens in front into a heat regenerator. The gas mixture passes from behind into the metal tube, through the catalyst and then through the heat regenerator into a circulating pump. Leaving this it passes in countercurrent around the outside of the regenerator tubes and the tube containing the catalyst and then enters this in front, repeating this journey again as described. The apparatus can be protected against loss of heat to the air by packing it in isolating material and can be enclosed in an outer shell which can withstand the pressure. The whole of the circulation takes place at high pressure. The catalyst is kept at the suitable temperature by electrically heating from within or by applying heat from the outside. Between the heat regenerator and the circulating pump the gases pass through either an absorber or a condenser for ammonia. By means of a branch tube the nitrogen and hydrogen combined to ammonia can be replaced.

Finally, it was a great step forward when Haber found catalysts with the property of rapidly combining nitrogen and hydrogen to ammonia in sufficient quantity even at much lower temperatures than those pre-

viously required. He found this to be especially the case with osmium. This metal has such a very favorable action, even at 550° C. and below, that under a pressure of 175 atmospheres a gas concentration of 8 volumes per cent of ammonia can be obtained. This was all the more astonishing, as platinum, which is closely related to osmium, has but a very slight catalytic action. For use on a large scale, however, osmium scarcely comes into consideration, for the world's stocks, according to Haber, do not amount to much over 100 kg., and only small quantities (about 1 kg.) are obtained annually; this quite apart from its high price and very unpleasant properties.

Very soon Haber found in uranium a further very good catalyst; it can be employed in the form of the metal, of an alloy, or nitrid, or carbid. In the form containing carbon or carbid, such as is produced in the electric arc from uranium oxid and carbon, it crumbles in the gas mixture under high pressure to a very fine powder containing nitrogen, which even under 500° C. has an excellent catalytic action. No water, however, or impurities which give rise to water, must be present in the gases when uranium is used in this way. From Table I, which shows the equilibria obtainable at different temperatures and pressures, can be seen the importance of the temperature at which a catalyst is active for the equilibrium of the ammonia produced.

TABLE I.
Equilibria ($N_2:3H_2$).

Temp. Degrees Centigrade.	Pressure.	
	1 atm. Per cent.	100 atm. Per cent.
800	0.011	1.1
700	0.021	2.1
600	0.048	4.5
500	0.13	10.8
400	0.48	..

Haber published a short report of his work in 1910.¹² To my great regret Professor Haber has not been able to accept the invitation of the officers of this Congress to report personally here on his researches, owing to being hindered by pressure of work. I have great pleasure in fulfilling his wish and thanking the officers of the Congress today for the honorable invitation and express his regret to this meeting that he is unable to be present.

I now turn to the work of the Badische Anilin- & Soda-Fabrik on the technical development of the process. This work was of course at once taken up in 1908 after the first communications of Professor Haber, and Dr. Carl Bosch was entrusted with it. In conjunction with his colleagues and with equal energy and experience in the field of chemistry and engineering he has successfully carried out the practical application of the process.

The problems to be solved were quite new and strange and demanded the mastery of very unusual difficulties. Although working with compressed gases under pressure at very low temperatures was already known in the industry, the problem here was the totally

¹¹French Patent No. 406,943.

¹²German Patent No. 238,450, September 14, 1909.

¹³Sketches in Haber's article in the *Zeit. für Elektrochemie*, 16, 244-5 (1910); and also British Patent No. 17,951 (1909).

¹⁴*Zeit. für Elektrochemie*, 16, 244-5.

different one of constructing apparatus which should be large enough and at the same time able to withstand the high pressure with temperatures not far from a red heat. How well founded were the doubts as to the possibility of a solution of this task can be gathered from the instance of the wrought iron autoclaves commonly used in the color industry. Here, in spite of a very low range of temperature of at most about 280°C ., only pressures of from 50 to 100 atmospheres at the utmost come into consideration. But above 400°C . iron loses its solidity to a very extraordinary degree.

There is further the circumstance that the metals which come into consideration for the construction of the apparatus, and especially iron, are chemically attacked above certain temperatures by the gas mixture under pressure. Although the formation of iron nitrid from iron and ammonia, which could have been expected according to the work of Frémy and others, can be avoided, yet it is found, for example, that steel containing carbon loses its carbon at the temperatures in question owing to the action of the hydrogen, so that its capability of withstanding pressure is reduced to a minimum. It was further found, when using iron itself, that it is completely changed in its qualities, chiefly by taking up hydrogen. Again, at such high temperatures iron is pervious to quite a remarkable degree to hydrogen under high pressures. The question of materials for the apparatus, therefore, raised at once considerable difficulties, but at length these were more than overcome by suitable construction, details of which, I am sure, you will not expect from me today. The danger of serious explosions or of great sudden flames of hydrogen, if the apparatus happens to become defective, can be guarded against by setting it up in bomb-proof chambers.

Great care must naturally be taken that oxygen or air does not get into the apparatus or the piping, for at the high pressure obtaining the explosion range is reached with merely a slight percentage of oxygen. Special devices are used to watch over this content of oxygen, and immediately a definite percentage is touched the alarm is automatically raised. Besides this the proper constitution of the gas mixture in circulation is controlled by analysis from time to time.

The ammonia can be removed either by being drawn directly from the apparatus in liquid form, or an absorption agent can be suitably introduced into the apparatus. The simplest absorbent, water, has been found to be suited for this purpose; under the pressure used a concentrated solution of ammonia is secured. Any ammonia that may remain in the gas after the bulk has been removed by one or other of these methods can be further removed by special chemical means, if it is not preferred simply to leave it in the circulating gases.

As before mentioned, Haber observed that there are contact agents which are much more active than those previously known (osmium and uranium being indeed

found to be much more active than pure iron prepared from oxalate of iron or oxid of iron, platinum, pure manganese, chromium and nickel, already at considerably lower temperatures). The Badische Anilin- & Soda-Fabrik, therefore, decided to study the various catalysts very minutely.

In the course of these investigations, the new fact discovered, that ammonia catalysts in general are made more active by the presence of certain foreign bodies, has proved to be of prime importance. Among these "promoters," as they have been termed, are oxids, hydroxids, or salts of the alkalies, of the alkaline earths and the earth metals, further many other substances of the most varied nature, especially other metal compounds or metals themselves. In many cases just a minute quantity suffices to raise the catalytic activity. This trait is common to all catalysts, for there is not one but its activity can be raised by these means. Care must, however, be taken (for reasons to be discussed later on) not to choose such mixtures that metalloids, such as sulfur, selenium tellurium, phosphorus, arsenic, boron, etc., under the conditions prevailing, are incorporated in the catalyst. Similarly, compounds of metals with a low melting point which are readily reduced by hydrogen and which themselves do not act as catalysts must be avoided; such metals themselves as lead, tin, zinc and bismuth must also not be added.

The promoters mentioned can be added either to the prepared catalyst or to the substances used in its preparation, or the catalyst can be prepared from such materials as already contain such additions in suitable mixture (for example, magnetic ironstone). Under certain circumstances the action of these foreign bodies is specially powerful, *viz.*, if the metals, or oxids, or carbonates, or other compounds which are converted into oxids on heating, are first heated to high temperatures, preferably to melting point, and so that the resulting product consists chiefly of oxids. When proceeding in this way with metals, for instance, iron, of course sufficient oxygen or oxygen-producing compounds must have access. The mass of oxids obtained as described is suitably broken up and filled into the contact stove either directly or after reduction. In this case extremely small quantities of foreign substances suffice to secure a high and continuous activity of the contact mass.

We consider the marked activity of catalysts prepared in this way to be in the first place due to the fact that the additions mentioned dissolve, on heating, in the highly heated metallic oxid or become finely divided in it, and that in this way during the following reduction a sort of skeleton, which, however, is hardly to be detected, is formed inside the metallic mass. This effectually prevents a diminution of the surface, and therefore also of the catalytic properties of the mass.

It was then further found that good results can also be achieved with pure iron—that is to say, that we can work with it at temperatures of, for example, not much

above 600° C.—thus if the iron intended for the catalysis is prepared from the oxid or other iron compound at a comparatively low temperature, preferably not above 600° C. It can also be prepared by highly heating pure iron oxids, or pure iron in the presence of oxygen, preferably to melting point, and by reducing the mass of oxid preferably at a not too high temperature.

Also manganese, which is related to iron, gives under a specific condition good results without the addition of foreign substances. This condition is that care be taken to free completely the mixture of nitrogen and hydrogen, before it enters the contact space, from oxygen, either free or combined, for instance, as steam or water. Merely drying with calcium chlorid is not sufficient. In the case of several other catalysts, too, a similar careful drying has proved to be useful.

Again, it has been found that another member of the iron group, molybdenum, is by itself an excellent catalyst. Compounds of molybdenum can also be used, for instance, molybdic acid or ammonium molybdate.

Under certain conditions, not published as yet, tungsten, either the metal itself or as an alloy or a nitrogen compound, has been found to be a suitable catalyst.

In view of the shortness of the time I must refrain from a more exhaustive discussion of this most interesting chapter of the contact bodies. It will be quite evident from what I have said that the industry has now a number of active contact bodies for the synthesis of ammonia at its disposal, and can select from case to case the most suitable.

Another discovery of first-class importance for the industrial application of the catalysis of ammonia was the recognition of the fact that there are special poisons, so to speak, for the reaction. That is to say, there are substances which hinder or prevent the reaction, although the contact mass does not suffer a noticeable chemical change, envelopment or destruction. In the literature there was no indication whether there were poisons at all for the contact mass in the catalytic manufacture of ammonia, or what their nature would be. In actual manufacture such contact poisons were known only in the case of the catalysis of sulfuric anhydrid, and even here only when platinum was used. When employing other contact bodies, such as iron oxid, or burnt pyrites, there was nothing known of contact poisons; on the contrary, it has even been shown that the presence of arsenic, which is a poison for platinum, has actually a favorable action when iron oxid is used as catalyst.

It has now been ascertained that some of the poisons in the syntheses of ammonia are of quite a different nature from those of the sulfuric acid process; they are, for instance, sulfur, selenium, tellurium, phosphorus, arsenic, boron, or the compounds of these elements, such as sulphuretted hydrogen, arsenic hydrid, phosphorus hydrid, as also many carbon compounds and certain metals of low melting point which can readily be reduced by hydrogen from their com-

pounds, for example, lead, bismuth and tin, which do not act catalytically. Oxygen-sulfur compounds, such as SO₂, which acts directly and smoothly in the sulfuric acid catalysis, are very poisonous. Extremely minute quantities of these bodies, which are almost always present even in the purest commercial products or in the so-called pure gases, suffice to render the catalysts absolutely inactive or at least to diminish their action very seriously. Thus iron, for example, prepared from ordinary iron oxid with a content of one per thousand of sodium sulfate is, as a rule, inactive. Iron containing one-tenth per cent of sulfur is generally quite useless, and even with one-hundredth per cent is of very little use, although in appearance and when examined with the ordinary physical and chemical methods no difference at all can be detected as compared with pure iron.

The recognition of these facts gave rise to two problems:

(a) The preparation of contact masses free from poison or the removal of such poisons from them.

(b) Freeing the gases to be acted on catalytically from all contact poisons.

In order to free the contact bodies from these harmful substances the ordinary methods for removing them can of course be applied. The contact action can also be improved by heating contact metals which are inactive or of little use, owing to the presence of contact poisons, in the presence of oxygen or of bodies yielding oxygen. Or the metals can be heated, for instance, in the presence of oxygen with the addition of suitable compounds such as bases, and the resulting products reduced. These operations can be repeated if necessary. If more of such a body as mentioned is added than is necessary, it may act not merely by removing the poisons, but promote the yield, as I have already described to you.

On the other hand it is necessary, as I remarked, to take the greatest care that nitrogen and hydrogen are free or freed completely from all contact poisons. Thus a trace of sulfur, one part per million, in the gas mixture can under certain conditions be injurious, so that even electrolytically prepared hydrogen must generally be further specially purified. The minute purification of the gases is even more important when hydrogen prepared, for example, from water gas is used. The impurities, too, taken up from iron piping play sometimes an important part, and impurities which get into the gases during the compression, such as machine oil, often have a harmful effect.

The best method of removing impurities from the gas mixture depends in turn on the nature of these impurities and consists, for instance, according to the case, in filtering, washing, conducting over solid absorption agents, and so on. One good method is to bring the gases into contact with the material of which the contact mass is prepared at a raised temperature before passing them over to the actual catalyst. The material takes up the impurities, and must of course

be renewed from time to time. The negative results of earlier investigators in the formation of ammonia when using base contact metals (Wright, Ramsay and Young, and, more recently again, 1911, Neogi and Adhicary), according to which nitrogen and hydrogen do not combine in the presence of iron, are in my opinion probably due, for the most part at least, to the use of metals or gases not free from contact poison. That previous inquirers had not the remotest idea that sulfur in the contact metal could be injurious is evident from the fact that they passed the gases without hesitation through concentrated sulfuric acid in order to dry them. The sulfuric acid thus taken up and the sulfur dioxide often contained in it can poison even the best catalyst very speedily and render it unfit for use. Or the contact metals were sometimes prepared directly from the sulfates, although a metal sufficiently free from sulfur can scarcely be obtained by this method.

A painstaking study, for which we are indebted principally to Dr. A. Mittasch and which involved literally many thousands of experiments, has afforded an insight into the importance of substances of the most varied nature as promoters and poisons and thus a sure foundation has been prepared for a reliable continuous manufacture with a good yield of ammonia.

The question has not yet been touched upon in the foregoing how the elements nitrogen and hydrogen which are requisite for the new ammonia process can best be produced on a technical scale. Theoretically, the task would be unusually simple. If you remember that the terrestrial atmosphere, according to the studies of A. Wegener and others, consists of practically pure hydrogen at a height of about 120 kilometers, indeed at a height of about 70 kilometers consists of almost exactly one volume of nitrogen and three volumes of hydrogen, besides a trace (about one-half per cent) of oxygen, you will understand that all the conditions were given for an ammonia factory, according to Jules Verne. For it would then merely be necessary to suck down the gases from the higher strata of the atmosphere by a sufficiently long pipe line.

For us, poor mortals, matters are not so ideally simple, for as the poet says,

"hart im Raume stossen sich die Sachen."

Fortunately, however, there is no great difficulty in separating nitrogen from the air, either by physical means, according to Linde's process, or chemically, by removing the oxygen with glowing copper, burning hydrogen, or the like. And for the preparation of hydrogen in recent times a great deal of useful work has been done, too, owing to the extensive growth of its field of application. In certain works it is at disposal in large quantities as a by-product of the electrolysis of common salt. Besides this it can be produced, for example, by passing steam over red-hot iron, or from water gas, for instance, by separating its constituents hydrogen and carbon monoxide by cooling to a very low temperature. All the methods of preparation

which come into consideration we have of course minutely examined; owing to the comparatively trifling differences in the cost of production various methods can be employed. At all events, both elements, nitrogen and hydrogen, are at the disposal of the new industry to any extent and sufficiently cheap.

Year.	Chilian export. ¹	Price ² per ton.	Total value. Marks. mil. M.	Increase.
1900	1,454,000	162.2	216.6	1901-11 995,400 tons that is an annual average of 99,500 tons containing 15.5 per cent. i. e., about 15,400 tons nitrogen, valued at 19 million marks.
1901	1,274,000	172.8		
1902	1,379,200	176.2		
1903	1,457,600	178.4		
1904	1,479,100	196.2		
1905	1,652,200	204.8	338.2	
1906	1,731,800	215.0		
1907	1,653,600	214.4		
1908	2,052,400	193.3		
1909	2,133,900	184.5	393.7	
1910	2,334,000	177.6		First six months 1912 150,000 tons valued at about 29 million marks as against corresponding period 1911.
Jan-June 1911	(1,299,000)			
1911	2,449,000	190.7	467.2	
1912	(1,449,000 ³)			

¹ According to the figures of the Association Salitrera.

² Annual average Hamburg quotations.

³ Semi-annual deliveries in Europe.

Year.	World pro-duction. Tons.	Price per ton. Marks. mil. M.	Total value.	Increase.
1902	543,000	211 ¹	1131	1908-11 329,000 tons, i. e., an annual average of 110,000 tons, containing 20.5 per cent. i. e., about 22,500 tons nitrogen, valued at about 30.6 million marks.
1908	852,000	237	202	
1909	978,000	230	225	
1910	1,111,800	248.5	276	
1911	1,181,000	278	328	

¹ Quotations f. o. b. Hull.

As the production of these elements is not confined to the presence of cheap water power, all those countries where the manufacture of calcium nitrate, owing to the want of such power, is not practicable, as for instance in Germany, are now in a position to profit by the new industry. As I remarked at the outset, there is every reason to assume that this industry will find a fruitful field of employment in America, where the demand for nitrogen manures will soon be greater than hitherto.

It can also be regarded as certain that the development of this new industry will not take place at the cost of other branches of industry and commerce. Bear in mind for a moment the present annual requirements for nitrogen manures and their continued growth. According to the tables before you, these figures reached the remarkable total of 467.2+320—i. e., 793.2 million marks (about 100 million dollars)—in 1911, and each year sees an increase. In the last few years the increased demand for ammonium sulfate amounted to about 10 per cent. The increase of production from 1910 to 1911 amounted to 60,000 tons, and from 1908 to 1911 on the average as much as 110,000 tons, or 110 million kg., valued at about 30.6 million marks (7.3 million dollars). Similarly, the nitrogen requirements of the world for manure purposes in the form of saltpeter is growing. Chili exported in 1908 about 2,052,400 tons of saltpeter, and already in

1911 the figure was about 2,449,400 tons—that is, an annual increase of nearly 150,000 tons, valued at approximately 29 million marks (7 million dollars). Indeed the European deliveries, according to the latest reports, from January to the end of June, 1912, reached as much as 1,449,000 tons, a demand which Chili was hardly able to meet. The average annual increase from 1901 to 1911 amounted to 99,500 tons. That is to say, taking saltpeter and ammonium sulfate together and reckoning only the average increases, calculated on nitrogen, we have an annual increase in production of about 38,000 tons nitrogen, corresponding to nearly 185,000 tons of ammonium sulfate.

It can thus be seen what enormous quantities of synthetic ammonium sulfate must be produced to affect the total production by as much as one year. The saying, so often applicable, that

"Das Bessere ist der Feind des Guten,"

will thus probably have no meaning in this field. A peaceful development of the various new industries for the combination of the nitrogen of the air side by side is to be expected, and without encroaching at all on the previous production of nitrogenous manures a favorable horoscope may be cast for a fortunate career for the new industry.

FIFTH ANNUAL MEETING OF THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

The fifth annual meeting of the American Institute of Chemical Engineers is to be held Dec. 4-7 at the Hotel Cadillac, Detroit, Mich. The program of the meeting is as follows:

WEDNESDAY, DEC. 4, 1912.

9:30 a. m.—Meeting at Hotel Cadillac.

Address of Welcome, Hon Homer Warren, P. M.

Business session—

Canvass of ballots for officers.

Reports of officers and council.

Reports of committees.

11:00 a. m.—Reading of papers.

Changing Rate of Setting Portland Cement, Prof. E. E. Ware.

Industrial Efficiency, Wm. M. Booth.

Technical Accounting and Chemical Control in Sugar Manufacture, David L. Davoll, Jr.

1:30 p. m.—Excursion.

It is understood that Chemical Engineers who are allied with competing companies will not attend these excursions unless they so declare themselves and extend the same courtesy of inspection from their own plants.

Parke Davis & Co.

8:00 p. m.—Meeting at Hotel Cadillac.

Presidential address, "Protection of Intellectual Property in Relation to Chemical Industry," Dr. L. H. Baekeland.

Availability of Blast Furnace Slag as a Material for Making Brick, Prof. A. E. White.

THURSDAY, DEC. 5, 1912.

Excursions—

Acme White Lead & Color Co.

Ford Motor Co.

Luncheon.

Pennsylvania Salt Mfg. Co.

Arrangements for automobiles have been made by the Society of Detroit Chemists and the local committee to take members of the Institute and their guests to these plants.

7:00 p. m.—Subscription dinner at Hotel Cadillac, \$3.00.

FRIDAY, DEC. 6, 1912.

8:15 a. m.—Train for Ann Arbor, Mich.

Inspection of laboratories and buildings of the University of Michigan.

12:30 p. m.—Complimentary luncheon at the University of Michigan.

1:30 p. m.—Papers.

The Chemical Engineering Laboratory of Columbia University, Prof. M. C. Whitaker.

Industrial Fellowships, Prof. Robt. K. Duncan.

Tests on the Opacity and Hiding Power of Pigments, G. W. Thompson.

Composition of Glucose and Starch Sugars, Dr. Edw. Gudeman.

4:50 p. m.—Train leaving Ann Arbor.

8:00 p. m.—Session at Hotel Cadillac.

Solvents for Acetylene, J. H. James.

Rotary Kiln Lining for Burning Portland Cement Clinker of Unusual Composition, Chas. A. Newhall.

The Bituminous Rocks of the United States and their Use for Street Surfaces, S. F. Peckham.

Final business session.

SATURDAY, DEC. 7, 1912.

Excursion—

Berry Bros., Ltd.

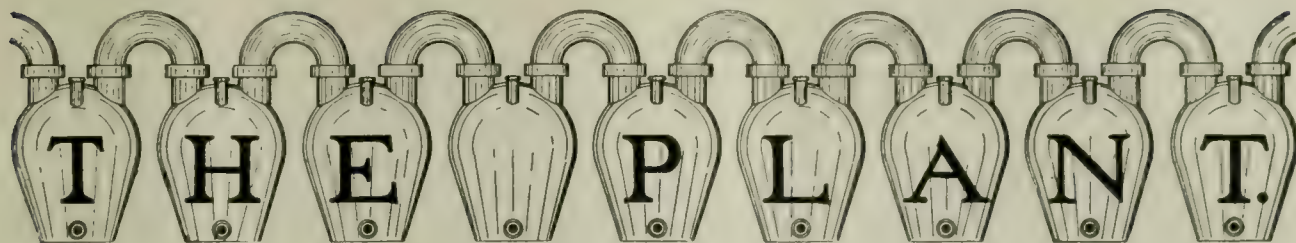
Permits have also been obtained for the following excursions:

Detroit Sulphite Fibre Co.

Detroit Copper & Brass Rolling Mills.

Michigan Malleable Co.

At a recent meeting of the Institute of Metals, Alexander E. Tucker of Birmingham called attention to the modern use of electric welding in manufacturing hollow ware, which involves a great saving of time and labor. Two forms of machines are designed, one for spot, the other for butt welding. In the spot-welding machines the sheets are joined at spots where normally rivets would be used, electrodes being shaped according to the work to be done. An unskilled workman can make 1,000 welds per hour on plain sheets where an expert worker could only put in 240 rivets in the same time. This process is supposed to give greater mechanical strength and permanency.



ARTIFICIALLY SOFTENED WATER FOR FOOD PURPOSES.

By WM. M. BOOTH.

Until recently mineral and sanitary analyses of water have seldom been required by manufacturers in the United States. If a supply was found unfitted for its use, another source was substituted or the industry was moved to a new location. In some instances great financial loss and even failure of an enterprise may be traced to a bad water supply. Little attention, comparatively, has been paid in this country to the separation of suspended and dissolved matter from water, although apparatus for this purpose has been used quite generally in England and Germany for 50 years.

In my own experience, a dye house was moved from one plant to another many miles away because better results could be obtained in setting colors in cotton yarn at the latter place. A thriving city lost an industry and the manufacturer lost considerable money. No attempt was made to soften the supply.

In another instance, two paper mills regularly suspended operations after a heavy rain owing to muddy water. These plants were idle hours at a time when a mechanical or sand filter would have effectually clarified the water.

There is a canning factory in western New York that cannot be operated because no good water could be found after the plant was located and started. Many other instances might be cited showing the necessity of a thorough investigation of water conditions before a plant is located.

The eastern and middle states are becoming so thickly populated and manufacturing concerns so numerous, that water exactly adapted to the needs of an industry is an exception. It has become necessary to correct irregularities of the supply by aeration, filtering, sterilization, distillation or chemical treatment. In some instances, the same water is now treated with alum, dosed with hypochlorite of lime and softened with lime and soda. The problem is so complicated and the demand so urgent that chemists, engineers and bacteriologists have combined forces to effect its solution.

To show what has been done in a single industry to correct a water supply, I have chosen the use of softened water in canned goods.

It has been found that peas and certain vegetables are hard and tough when preserved by syrup made up with hard water and that they are soft and palatable when cooked with water free from mineral matter.

During the spring of 1904 one of my clients asked me to consider the advisability of installing a water softening system in connection with the preparation of syrup for canned goods. I objected to the use of such water for the purpose intended and gave as my principal reason the possibility of an overdose of chemicals in the tinned goods with probable action on and solution of the tin itself. Distilled water had been used exclusively by a food concern for which I served as chemist and such water was recommended in this instance. A report was made on the cost of a distilling plant with the necessary pumps. This initial expense was considered excessive as was also the operating cost. Five thousand cases of 24 cans each were put up daily at this cannery. This output called for the use of a 60 H. P. boiler ten hours per day. At that time, a boiler in that plant could not be run a single day without scaling badly. Everything considered, the distilled water idea was abandoned and a lime-soda purifier was purchased and installed, capable of taking care of 300 H. P. boilers with ample supply for blanching and syrup.

The raw water analyses were as follows:

	Parts per million
Total solids	1,115
Chlorine	trace
Calcium oxide	223
Magnesium oxide	75
Sulphur trioxide	438
Hardness	442
Alkalinity	170

About 16 grains of sodium would remain in every gallon of this water softened. The probable effect on canned goods was to me, at this time, questionable. Correspondence was begun with persons familiar with the use of softened water for drinking purposes and it was shown that some localities in the west produced waters that contained more than 200 grains of sulphate of sodium per gallon, and that such water was used by the natives with no ill effects.

While the process proved satisfactory, the apparatus did not. This was so designed that it was necessary for an employe to stir the cream of lime during the entire day, turning this from tank to tank and finally allowing the lime water to react with the soda on the raw water. With every precaution, it was found impossible to proportion lime and soda correctly. The softening process was only partially carried out and the natural water, with 26 degrees of hardness, Clark, was softened to 20 degrees, Clark, but this did not accomplish the purpose intended which included blanching and the boilers.

I was again asked to devise some method to improve

the lime-soda mixing apparatus. This was done by means of a weir which I had used elsewhere and found excellent for the purpose. The weir was provided with three outlets, one taking the main portion of the water the second and intermediate portion passed into the lime saturator, while the third was led to the top of the soda solution, driving the latter into the mixing tank. The canning plant had so increased in size that more than double the amount of water first used was now required and a mechanical stirrer for incorporating the lime and soda was found necessary.

I designed a tank and bucket contrivance which thoroughly mixes the lime and soda and at the same time dips out a portion of the material in suspension and solution where it is carried by gravity to the tank beneath mixing with the raw water during its course. This apparatus has been in use three years. It has been found that it is necessary to remove the gypsum only. This keeps the peas soft and the boilers clean. Although one large pump supplies the entire factory, the pressure is constant enough at the filter house to maintain the hardness of the purified water with a variation not greater than two grains per gallon during the entire day. Tanks and buckets are so arranged that a new charge is added once in ten hours. At this time, the residual lime which may amount to 10 lbs. and which consists of carbonate and hydrate is sludged out by a stream of water through the bottom. The valve is then closed and the tank filled with water. This takes about ten minutes. The stirrer is started and 270 lbs. of chemicals are added. The lime and soda are soon uniformly distributed and the softening process is begun within fifteen minutes from the time the apparatus was stopped.

By means of a float system and automatic electric switches the flow of the water and the stirring process are carried on uniformly. One hundred thousand gallons of water are treated daily.

For the past two seasons I have kept a record of the hardness. Some of the results follow:

Received.	Hardness.
July 19.....	214.20
July 20.....	153.00
July 21.....	187.00
July 22.....	211.40
July 23.....	241.40
July 25.....	243.10
July 27.....	249.90
July 28.....	255.00
July 31.....	197.20
Aug. 22.....	204.00
Aug. 25.....	221.00
Aug. 26.....	224.40
Aug. 28.....	170.00
Aug. 31.....	226.10
Sept. 2.....	221.00
Sept. 7.....	217.60
Sept. 8.....	231.20
Sept. 13.....	170.00
Sept. 14.....	170.00
Sept. 15.....	136.00
Sept. 16.....	170.00
Sept. 19.....	168.3
Sept. 20.....	168.3
Sept. 23.....	175.95
Sept. 26.....	165.75
Sept. 28.....	162.35
Sept. 30.....	173.40

These figures cover different classes of vegetables which it has been found by experience require a different degree of softening.

Last season a prominent canning company purchased new property and prepared to do a large business in peas and corn. The plant is very well located, as far as shipping facilities are concerned and is surrounded by excellent farming land. The canned goods ought to be produced at this plant economically and of good quality. The water supply was not considered, as canal and river are near, but both carry sediment and the water is hard. Several wells were driven to a depth of about 70 ft. Plenty of water was found but this, after standing a few hours, developed a brown precipitate which made it totally unfit for the purpose intended. With the canning season near, it was thought best to obtain a water survey of the property and chemical and bacteriological tests were made from all sources of supply. The mineral analyses are shown in Table I:

	Parts per million.							
	River.		Wells.					
	Canal.	A.	B.	C.	D.			
Total solids	630	358	2,170	4,880	3,006	3,780		
Sulphur trioxide	92	62	720	1,801	1,233	1,716		
Calcium oxide, sol....	39	...	...	...	...	...		
Calcium oxide, ins....	97	87	550	770	747	750		
Magnesium oxide, ins.	40	21	86	105	95	106		
Oxide, iron and al....	12	14	84	trace	trace	trace		
Hardness	356	168	980	1,260	1,260	1,227		
Alkalinity	233	147	275	89	190	111		
Free CO ₂	55	8.8	44	16	28	6.6		

The canal water is most available but it is not constant either in quantity or quality. This level is sometimes drawn off by intent or accident and the feeders east and west produce waters of unequal hardness. The river water, only, could be used for the purpose intended. In its natural condition this was both muddy and hard.

Upon inquiry it was found that large wooden tanks of 2,000 gals. capacity each were stored at another plant of the company. These were immediately shipped to the factory in question and two of them were set up on steel girders in a 25 ft. bay. Two other tanks were set immediately under these. Those above were provided with stirring apparatus and excelsior filters were built up in the tanks below. By working night and day the outfit was started three days from the time the order was given to ship the tanks. The new excelsior at first darkened the filtered water with resins and the first two runs had to be thrown away. The soft water plant was only capable of taking care of the needs of the factory by being run 24 hours per day. This was accomplished by placing a night and day man in charge. Four hours after the tanks have been filled and charged, the water is filtered. One and a half hours are allowed for the latter process. A new lot of water is then admitted; the stir re-started and the slacked lime added, the soda soon afterward, very slowly. The water analyzes as follows:

	Parts per million
	Hardness.
July 3, unpurified	356
July 3, purified	70
July 4	70

July 5	68
July 6	70
July 8	67
July 9	76
July 10	65
July 11	52
July 12	95
July 13	50
July 15	85
July 17	97
July 18, unpurified	393
July 19	61
July 20	67
July 23	81

The softener and filter have proved very satisfactory and at no time has an excess of chemicals reached the canned goods which have been examined daily for caustic alkalinity. Such results are only obtained by strictly following the chemist's directions.

Besides reducing the hardness, the filters remove the mud, leaving the water transparent and with little sediment.

Our experience with softened water in canned goods has extended over a sufficient period to warrant the conclusion that the lime-soda process can be used to good advantage to correct a bad supply. The products from the factories mentioned in the foregoing article are highly considered by the trade.

The U. S. Consul at Reichenberg, Austria, states that much interest in manifested in the Bohemian linen trade by a reported invention from the Russian textile industry. According to the information, an engineer at Moscow has produced chemically finer linen yarn than the finest yet spun; also that less waste is made in spinning process, thereby lowering the cost of production. Very fine linen goods are to be woven from the new yarn, the cost of which is calculated to be 20 per cent less than the finest articles of linen heretofore placed on the market.

Reports from the German artificial silk consuming centers state that orders for new season's goods made from this product are now coming in, and, according to a U. S. Consular report, the price of artificial silk has been steadily rising during the past 12 months, and it is impossible to buy at less than 13 marks per kilo (\$1.40 per pound) from any of the leading makers. Last year prices for best grades fell as low as 11 marks per kilo (\$1.19 per pound), and, although this may be a trifle above producing cost in the case of cupro-ammonium and viscose artificial silks, it is doubtful whether even the Belgian makers of the gun-cotton variety were selling without loss. Although the actual manufacturers of artificial silk have succeeded in obtaining the advance which has lately been more marked, doublers do not appear to have been so fortunate. This operation is largely carried on by owners of small plants, and such is the competition among them that consumers of doubled yarns are frequently given the advantage of any cheap contracts made by the doublers, with the result that prices are depressed all round.

WATER PURIFICATION AND ITS APPLICATION TO INDUSTRIAL USES.*

By H. ROYAL-DAWSON, F. C. S.

Water needs to be purified according to the purpose for which it is required, and this must be done chemically, either to soften a hard water or to harden a soft one. It has been the author's experience to note the great difference there is in a supply of soft water and that of a hard nature in making the same product. It showed a very marked contrast, which was only found out by constant analytical research. On this account the writer of this article hopes that what is herein stated may enable many users of water to go into the matter and watch their source of water supply as carefully as they look after their finished products.

The equality of a water and its adaptation to a special industry is chiefly to be noticed in that of brewing, where much capital would be lost if the water supply were not constantly under the control of a trained chemist.

Again, certain substances which do not affect the water for household purposes render it useless for some trade uses, and, on the other hand, some substances that render water so disagreeable to the taste may not be disadvantageous for some factories. Let us take these two instances, and note how much they differ:

CONDITIONS FOR DRINKING WATER.

- (1) It must be clear, colorless, and odorless when made lukewarm.
- (2) It should contain little or no organic matter, and absolutely no bacteria to set up putrefaction or disease.
- (3) It should contain no large amount of ammonia, no nitrates, sulphates, or chlorides to any extent.
- (4) It should not be too hard.

Well waters should show no signs of ammonia or nitric acid whatever.

A soft water for household purposes should contain that amount of lime sufficiently in quantity as to prevent chemical action taking place. Distilled water, or soft river water rapidly acts upon lead, and many cases of lead poisoning have occurred in consequence of persons drinking waters which have been in contact with lead, of which service pipes are mostly constructed. Sand filters do not remove lead, but if about one to two grains of sulphate of lime be added to each gallon of water, it would solve the problem, and render the water sufficiently hard to resist the lead dissolving in it.

CONDITIONS OF WATER FOR INDUSTRIAL PURPOSES.

(1) WATER FOR STEAM BOILERS.

In order to prevent formation of boiler scale, water for steam boilers should contain little carbonate of lime, and very little magnesia. To make the water suitable if of a hard nature, it should be purified by a softening process before being put into the boiler. Moreover, water containing much dissolved air and

*From the Chemical Trade Journal and Chemical Engineer.

carbonic acid acts on the boiler plates. Chlorides, if in any excess, are likely to form a rust deposit, and it is a good plan therefore to heat the water prior to feeding the boiler, and thus reduce the scale formation to a minimum.

Grease and oil of condenser waters containing them are very deleterious. There is a great risk of forming a ferro-calcium soap under certain conditions in the boiler, which, as it continues to spread in a thin layer over the plates, prevents the water from reaching the metal, thus setting up a reaction, causing the boiler plates to wear out in a short space of time. To overcome this, mineral oil, such as petroleum, should be sprayed over the boiler plates. A very handy book on the subject of "Boilers and Boiler Control" is published in a popular form, and should be studied by the chemists of all industries which depend so much on the production of steam for their various chemical plants, and which would be the means of saving a heavy expenditure for fuel where steam is so much required. A full analysis of boiler scale would give a fair indication of the kind of water being used, and is an interesting record, especially in that of steamship boilers, where condensed sea water has to be used for steam production.

(2) WATER FOR BREWERIES.

The water here should contain little or no organic matter and be entirely free from all organisms likely to bring about a false fermentation. A knowledge of the bacteriology of water is a great essential in the brewing room, and would be a splendid adjunct to chemists employed in this industry.

But from the side of inorganic chemistry, water for brewing should be a good drinking water, moderately hard, and not containing iron. This ingredient tends to darken the roots after a boiling with hops. If the source is from a private well, which is often the case, the water, if deficient in lime salts, should be previously treated by running through tanks built of slate and filled with rock gypsum. Filtration from suspended matter previous to this treatment is recommended.

(3) WATER FOR DISTILLERIES.

This is the same as is used for breweries, except that an excess of sodium chloride renders it unsuitable for the germinating process, and magnesium chloride is still more unfavorable.

(4) WATER FOR TEXTILE INDUSTRIES.

Water for this industry should be clear and colorless. Iron has a deleterious action, discoloring the fabrics, etc. Hard water should be avoided, except when used in the process of spinning raw silk. Lime is also an essential for certain industries, such as Turkey-red and coal tar colors.

(5) WATER FOR TANNING INDUSTRIES.

Great care should be exercised here, and a knowledge of bacteriology would be of assistance rather than water analysis only. Organic matter is detrimental, as it is inclined to set up "leather rot," or decay. Leather

should be swelled in water that contains sulphate of lime and magnesium. Iron of necessity is dangerous, as it gives the leather a dark appearance in color when tanned.

(6) WATER FOR MANUFACTURE OF HEAVY CHEMICALS.

Water for this industry needs as much attention as in any other, for in the manufacture of heavy chemicals, where cleanliness and purity of the product are required, a hard water will not serve the same purpose as a soft water. Take, for instance, sulphuric acid; chlorides should be eliminated, and so for hydrochloric acid it is essential that sulphates should be reduced to infinity, if possible; therefore, for absorption a soft water should be given preference to one of a hard nature.

There are other industries that require as much thought and attention as those mentioned (for instance, the sugar and starch industry), but space will not permit to enumerate the qualities best suited for these. From the above examples it is quite obvious that there is a great difference to be seen, and it is only by chemical treatment in adding or subtracting a substance in order to purify it for its particular purpose that a true standard can be arrived at, to always keep a product, or industry, systematically under continual chemical control, checked by periodical tests in the laboratory.

Having generally discussed the various qualities of waters for industrial requirements let us now turn to the matter of

PURIFICATION.

This is undertaken in many ways, but common to all, by the use of sand filters, after its treatment chemically or by bacteriological means. Sand filtration is the best means for keeping away any germinating bacilli. When a new filter is started the water is not allowed to pass through for consumption until it runs fairly bright and clear. In due time a jelly-like formation takes place on the surface of the sand, and this acts as a media for all bacteria, and the purity is at once asserted, but to remove or disturb this glutinous-like mass means disaster to the water supply. For this reason all drinking water should be filtered for household purposes, and if attention were given to this more often, it would go a long way to eradicate disease.

House filters are constructed on the principle of sending water through a porous substance, such as charcoal, under pressure, which retains all suspended matter, purifies the water, and renders it bright and clear. But a bright appearance does not always imply a good water, and a test for chlorine and oxygen should be undertaken to certify the quality. Sand filtration first originated in England, and has now become general, everywhere abroad. The filters are formed in the following manner: First, drain pipes, then stones, which gradually diminish to the size of gravel, till the top layer consists of fine sand. The thickness of these filters depends a great deal on the amount of work they have to do on the quantity of

water required. All materials should be well washed and cleansed before being placed in position. Care must also be taken during frost in the winter months, when such filters freeze, causing fissures in the sand, and ultimately bad filtration.

Asbestos-cellulose is a good filter medium, and more easily cleansed than sand.

Purification by chemical means consists in the addition of lime, which precipitates the carbonates of the alkaline earths, and also the magnesium and iron which in turn causes other ingredients to settle.

The most frequently used agent for precipitating organic matter is sulphate of alumina, which carries down all floating impurities, and after settling produces a very clean filtrate. Care must be taken that no excess of precipitant is used as to injure the quality of the water.

Ozone is used on the Continent, and in time should become more popular in England for many purposes other than for potable waters. The oxygen of the air is converted into ozone by a silent electric discharge, which passes between metal electrodes, maintained at a high potential, but separated by glass to prevent sparking. The air, before passing into the ozonizers, is passed through a freezing machine in order to remove dust and moisture, and a concentration of about 2.5 grams per cubic metre of air is obtained, which is considered a suitable concentration for the after-treatment of the water. The movement of the air through ozonizers, and its intimate mixture with the water to be purified is effected, without the aid of pumps, by "emulsifiers," or injectors. From the emulsifiers the water is sterilized by passing through towers. The absorption of ozone, and its accompanying sterilization, occurs partly in the emulsifiers and partly in the towers. From these towers the water passes away over cascades, which remove the last traces of free gases and ozone into the storage tanks, and from here it is ready for the town supply.* Much research is needed whereby ozone could be used for other purposes than purifying water. Under German labor conditions the ozone treatment works out to 3½d. per 1,000 gallons.

PURIFICATION OF FEED WATER FOR BOILERS.

The greater the work put upon a boiler to do, the more should be the attention paid to the quality of its water supply, in order that it may continue its course without stay or hindrance, except being cleaned out at suitable times. To do this all boiler waters should be specially treated before entering the boiler, and thus save the formation of crusts," and consequent excess expenditure of fuel.

The chief idea is that the water may not form any incrustations or sediments of lime and magnesia salts. The deposits usually consist of carbonates of iron and magnesium, sulphate of lime, chloride of sodium, organic matter, fatty acids from lubricants, from which in former years the author has found ground for inter-

esting research in connection with boiler incrustations taken from steamships in the Thames. Incrustations are bad heat conductors, and consequently cause large consumption of coal, and if allowed to increase, without systematic cleansing, are the cause that often leads to explosions and other serious consequences.

The methods used to prevent the formation of "scale" or "crusts" may be divided into two classes, or headings—(1) mechanical methods; and (2) chemical methods.

The best way to keep a boiler as free as possible from sediment under the first method is by forcing air through it and greasing the inside with petroleum. A good way is to add petroleum to the water, and this directly avoids the formation of scale. Heavier oils are not to be recommended, as they tend to form fatty acids on dissociation at the high temperature and pressure at which boilers are worked. Fatty acids form a thick coat on the sides of the plant, and in time eat into and corrode the metal.

The general method is to use a mixture of soda and lime. The soda precipitates the lime salts as insoluble carbonate of lime, and the lime in a slaked form, or lime water, decomposes the bicarbonates. If the water be heated it can be purified by soda alone, when calcium sulphate is precipitated and the bicarbonates are decomposed by the heat. It is the custom nowadays to purify feed waters before they enter the boiler, and only such water as is clear and free from sediment should be used. If such treatment of boiler feed waters were systematically done, and put under proper continual chemical control, the cost of fuel for heating would be greatly lessened, and the life of a boiler would be no anxiety to the chemical engineer.

It is a good recommendation that the works chemist should include in his daily routine of ordinary tests outside the laboratory that of testing the water in boilers for acidity or alkalinity, and have a certain standard to go by. Glue gases also for CO₂ must not be forgotten. In this way a very good record is obtained as to the working of a boiler and its saving cost in fuel.

The management of the boiler in a works is of primary importance, as without a good pressure of steam always at call, chemical processes cannot be expected to work profitably, and this is obvious to all manufacturers of sulphuric acid by the chamber process.

PURIFICATION OF TRADE WASTE EFFLUENTS

The wide area that this section of purification covers will not permit of much being said on the subject, so it is intended to deal with only those substances that are purely inorganic, such as effluents from bleaching powder works, breweries, iron pyrites waste, tanneries, and brine works.

Where bleaching powder is made the drainage from the exhausted bleaching tanks consists of hypochlorous acid, and that from the neutralizing tanks contains sulphate of soda. By mixing, or running together, the two tanks, and adding lime, a precipitate is formed.

*The Engineer, December, 1911.

and after settlement the calcium chloride in solution is recovered, as it is injurious to fish life. The drainage from bleaching powder works can be used for seasoning timber, and for disinfecting main drainage. But if it is to be purified, this can be done by treatment with alkali waste, and then oxidizing with a little nitric acid.

The drainage from breweries varies considerably, but it chiefly comes from the "coppers," or boiling vats, consisting of hop refuse and soluble nitrogen compounds. The water hardly requires chemical treatment, being so dilute, but in case of necessity a mixture of lime and alumina is recommended.

Pyrites pits waste contains ferrous sulphate and sulphuric acid in the drainage water. By treatment with oxide of lime, crude gypsum could be obtained in the usual way.

The refuse water from tanneries contains decomposed animal matter. Sulphide of lime, and arsenic from the use of sheep dips, may also be found. In this case clarification with lime and sulphate of iron, and filtration afterwards, is to be recommended.

The refuse of the Leblanc Soda process, when dried, could either be used as a manure or worked up into other products. The waste effluents from the Ammonia Soda process contains much calcium and sodium chloride, and from these constituents hydrochloric acid and free chlorine can be produced.

Considerable developments are now contemplated and in progress throughout the French iron and steel industry, and prominent among these is an installation of two blast furnaces of 200 tons capacity, each measuring 25 meters in height and 7 meters in diameter, to be loaded automatically on the Stahler system, for the Société Senelle-Maubeuge at Longwy. The plant will include a cylindrical mixer of 500 tons capacity, a large Martin-Talbot open-hearth furnace of 200 tons, three 20-ton converters, and two horizontal blowing engines of 4,000 h. p. each. The output is estimated at nearly 19,000 tons of ingots a month. In the central power station, which is fitted with two turbo-alternators of 1,000 kw. and 1,700 kw., respectively, the addition of a gas-engine plant to work on blast-furnace gas for the generation of electricity to the extent of 7,500 h. p. is now being made. The installation of Jules Collart et Cie. of Steinfort, which has been acquired by the Usines et Aciéries de Steinfort, will be enlarged by the addition of two blast furnaces and a large steel works.

According to a bulletin of the U. S. Geological Survey, the anthracite mining industry of Pennsylvania has become concentrated into strong and relatively few units. It is stated that in 1911 nearly 75 per cent of the mines were producers of more than 100,000 tons each, and that 97 per cent of the total production of hard coal was from this group of mines.

OXIDATION OF ATMOSPHERIC NITROGEN AND DEVELOPMENT OF RESULTING INDUSTRIES IN NORWAY.*

By SAMUEL EYDE.

We all know that the atmosphere surrounding us is composed of nitrogen and oxygen; to create by the union of these two elements new chemical combinations that can be utilized in the world's household is the task of the new industry.

(The work of Priestley and Cavendish, Crookes and Rayleigh and Ramsay, and Lovejoy and Bradley along this line was mentioned briefly but with appreciation.) The difference between previous methods and that of Birkeland-Eyde is that the latter have applied large quantities of electric energy in the electric arc, and have first found out the best method of doing this, while it was previously believed that it was small quantities of energy that gave relatively the best results. It is on that assumption that the apparatus employed by them was constructed.

In the Birkeland-Eyde method, the electric flames used in the electric furnaces start between the points of the electrodes which are close to each other. By this an easily movable and flexible current is established, which, with the arrangements made, will be found in a highly magnetic field. The electric arc that has been formed moves on account of this magnetic field with great velocity perpendicularly to the lines of force, and the electric arc's foot draws back from the points of the electrodes. When the length of the electric arc increases, the electric resistance becomes greater and the tension increases until it becomes so great that the new electric arc starts from the points of the electrodes.

To regulate the current, an inductive resistance is used in series with the flame. With alternating current all the arcs are formed alternating in opposite directions and appear to the eye to be circular discs. This flame is a powerful technical means for the oxidation of the nitrogen of the air. The flame in our furnaces burns with a steadiness that is really astonishing.

The electrodes are thick copper tubing, through which water passes for cooling them. The chamber in which the flame burns is circular, of only a few centimeters width, and about three meters diameter.

The interior of the furnaces is lined with fire clay brick, through the walls of which the air is admitted to the flame. The nitrous gases formed in the flame escape through a channel made along the casing of the furnace, which, like the flame chamber, is furnished with fireproof bricks.

Each furnace is furnished with an induction coil, by means of which the power is regulated as required.

*From a lecture delivered by Dr. Samuel Eyde, of Christiania, Norway, at a joint meeting of the Sections on Inorganic Chemistry, Physical Chemistry, Electrochemistry and Agricultural Chemistry at the Auditorium of the American Museum of Natural History, Eighth International Congress, New York, September, 1912.

The induction coil serves to make the flame in the furnace steady even while working. This furnace burns for weeks without any regulation worth mentioning. The maintenance of the furnace and its repair are simple, as the most exposed portions, the electrodes, require change only every third or fourth week, and then only a small part of them, and the fireproof masonry every fourth to sixth month.

The temperature in our flames exceeds $3,000^{\circ}\text{C}$. The temperature of the escaping gases may vary between 800° - $1,000^{\circ}\text{C}$. The furnaces are made of cast steel and iron, the middle of the furnace being built out to a circular flame chamber. The electrodes are led radially into this flame chamber. By aid of centrifugal fans the air is brought into each furnace through tubes from the basement.

From furnaces no longer than could be held in the hand, and which took an energy of some few horsepower we have attained two types which can, as mentioned, take an energy of more than 5,000 H. P. We have had in the course of this period of developing our method four experimental stations.

Some years later than the invention of our furnace, Dr. Schoenherr, with the electrician, Hessberger, of the Badische Company, perfected an electric furnace for the oxidation of the atmospheric nitrogen, which is built on quite a different principle.

In place of the great disc of electric flame he develops a long slender arc in the axis of a narrow iron tube, through which a current of air is forced.

The type now used consists of a somewhat slender vertical column of iron plates seven meters in height. The inner tube is the reaction chamber; the others form channels for the entrance of the air current and its exit after coming in contact with the flame. In this way the heat of the outgoing gas is transferred to the ingoing current.

At the lower end is the main electrode, movable in a vertical direction. The reaction tube serves as the second electrode. By means of a lever the space between the electrode and the tube can be bridged over and the arc formed. The air current, forced by a powerful aspirator, enters in the lower part of the furnace and passes the channels. The entrance to the reaction chamber is through a number of small tangential openings arranged in several horizontal rows in the sides. The current passes in this way from the chamber and the arc is driven up in the midst of the rapidly moving current of the air.

As a quick cooling is of importance in securing a good yield, the upper third of the tube has a water-jacket through which the gases pass, and in this way the reverse reaction is prevented to a notable degree.

The reaction is identical with that obtained in the Birkeland-Eyde furnace, and the yield, as far as the results now obtained show, is practically the same.

At Notodden we have only furnaces of the Birkeland-Eyde system, from 1,000 to 3,000 kw.

At Rjukan there are, however, furnaces of the B.-E.

system, 3,000 kw., as well as furnaces of the Schoenherr system, all of 1,000 kw.

When the air in the flame chamber has been treated by the electric flames the nitrous gases formed pass out through pipes which convey the gas to the steam boilers, in which the temperature, which was, as mentioned, $1,000^{\circ}\text{C}$., is reduced.

The steam produced in the boilers is utilized in the further treatment of the products. In the boiler house there are also air compressors which supply compressed air for pumping acid and lye in the factory's various chemical department. The gases pass on from the steam boilers through an iron pipe into the cooling house. Each cooler consists of a great number of aluminum tubes over which cold water runs, while the hot gases pass through them and are considerably cooled. From the cooling chambers the gases go on to the oxidation tanks.

These oxidation tanks are vertical iron cylinders lined with acid-proof stone. The object is to give the cooled gases a sufficient period of repose in which the oxidation of the oxide of nitrogen may take place. The necessary amount of oxygen is present in ample quantity in the air which accompanies the gases from the furnaces. From the oxidation tanks, the gases, by blast engines, are led into the absorption towers. All the towers are filled with broken quartz, which is neither affected by nitrous gases nor by nitric acid. To assist the passage of the gases, there are centrifugal fans constructed of aluminum on each row of towers. The gases enter at the base of the first tower, pass up through the quartz packing, and by a large earthenware pipe into the top of another tower, then downward through the quartz to the bottom of the second tower, and so on until the air, relieved of all nitrous gases, leaves the last tower. Water trickles through the granite towers, and this is gradually converted into a weak nitric acid, while the liquid used in the iron towers is a solution of soda. The absorbing liquid enters the top of the tower and is distributed in jets by a series of earthenware pipes, so that the permeating gases come in immediate contact with the absorbing liquid. In the granite towers nitric acid is thus formed, and in the iron towers a solution of nitrite of soda.

The liquid emerges in a constant, even stream from the bottom of the towers, that from the granite towers running into the granite cistern. Hence it flows into the "montejus" which serve to pump up the acid, which has to pass repeatedly through the tower before it has become strong enough for the purpose for which it is intended. The "montejus" are worked by compressed air, and send the acid up into large stoneware tanks. From these jars the acid again runs through the towers as described. The "montejus" work automatically.

The iron towers are percolated, as already mentioned, by a solution of soda; otherwise the whole process is practically similar to that in the granite towers. The solution of soda, owing to its far greater

power of absorption, effects the separation of the last remains of nitrogenous gases from the accompanying air. Of the entire quantity of nitrous gases passed through the absorption system about 97 per cent is absorbed. The finished nitric acid from the towers, which has a strength of about 30 per cent, by volume, is collected in granite cisterns, from which it is drawn to what is called the "dissolution works." These consist of granite vats filled with limestone, over which the acid is poured. This drives off with violent effervescence, the carbonic acid contained in the limestone, while the nitric acid takes its place and forms a watery solution of nitrate of lime or calcium nitrate. The rest of the acid is neutralized in small towers filled with milk of lime, and is now pumped into vacuum evaporating apparatus. The object of boiling in vacuum is the great saving in the heat required.

The steam required for the evaporation is obtained from the steam boilers, heated, as before mentioned, by the furnace gases. The concentration of the nitrate solution in the evaporizing plant is continued until the specific weight of the liquid at an even temperature shows a content of 13 per cent of nitrogen. This solution is then sufficiently evaporated and can be pumped up into the solidification chambers, where it is conducted upon a revolving cylinder, cooled on the inside, where it stiffens so quickly that it springs off in small leaf-like pieces, which can be granulated in the crushing mill. The coarse powder so produced is raised by an elevator to a vat, from the bottom of which it is tapped into casks holding 100 kilos net weight.

The gas led into the iron tower forms with the solution of caustic soda a solution of nearly pure sodium nitrite. This is concentrated by evaporation in the same sort of apparatus as above, and is allowed to crystallize. The crystals are dried in a centrifuge and tapped into casks.

The barrels are made at our own cooper's shop and are lined with paper to guard against the damp.

Besides these two products, nitrate of lime and nitrite of soda, we have during the last years at our Notodden Works taken up the manufacture of concentrated nitric acid and of nitrate of ammonia, which products have already won a good reputation, and in comparatively large quantities are shipped to the U. S. A. and other countries.

We are, however, in our industry not confined to these products hitherto mentioned. We have possibilities for the development of a whole series of new industries.

Visitors to our factories are often under the impression that the works are not running at all. There is but little noise and hardly any workmen are visible. Indeed it is remarkable how few people are required to run the establishments in our industry. Comparatively large working forces are needed only in the packing and wrapping departments.

For the development of the atmospheric nitrogen

industry the question of water power is a vital one. Our industry cannot exist unless it can procure for itself cheap water power. There is hardly a country in the entire world that can boast of more favorable conditions in this respect than Norway, and the enormous rise of our industry must be attributed to a very large extent just to Norway's magnificent opportunities regarding the supply of the factories with water power. It must be borne in mind that Norway has not only her magnificent and high waterfalls, but that she has big lakes likewise in her mountains, allowing the construction of enormous natural reservoirs for leading the water to the power stations. Especially in the districts of our industry we enjoy most favorable conditions in this respect. The works now built are all situated in the southeastern part of Norway, in the Telemark River district.

The first works, the Notodden Nitrate Factories, are admirably situated at the lake of Hiterdal, about 50 ft. above the level. A short channel with a series of locks permits communication with the town of Skien, an important seaport at the head of the fjord. Under the present conditions vessels of 100 tons burden can ascend to Notodden. It is planned to enlarge the locks so as to allow the passage of seagoing vessels of 2,000 tons.

The Notodden factories, which now have about 60,000 H. P. working, get this power from two neighboring waterfalls, Lienfos and Svaelgfos. At Lienfos, about two miles from Notodden, a dam with a fall of about 55 ft. was completed in 1911. The volume of water is 75 cu. m. per second. The power station is equipped with four units, each of 5,000 H. P.

The Svaelgfos power house is situated above, about one mile from Lienfos. The volume of water is the same as at Lienfos. The dam secures, however, a fall of about 165 ft. A tunnel takes the water to the reservoir, from which four flumes cut in the solid rock conduct the water to the station where there are four sets of turbine generators, each of 10,000 H. P. The generators are capable of evolving 13,000 H. P., and rank among the largest units in the world.

The power of these two waterfalls is transmitted to Notodden by six separate lines. Each line consists of six cables twelve millimeters in diameter. The three-phase alternating current of 50 periods is transmitted with a voltage of 10,000.

A second power station at Svaelgfos is now under construction. As the normal volume of water by an additional regulation of distant lakes in the same watershed soon will increase to ninety cubic meters, in the new power station likewise two additional units of 10,000 H. P. each are built.

About 16 miles farther up the river the first regulating dam at the Lake of Tinn was constructed at the same time as the water station of Svaelgfos and the factories at Notodden. The immense basin regulated by this dam makes it possible to store up fully 300,000,000 cubic meters of water.

For the regulation of the water supply a dam was built at the Lake Mosvand by means of which the level of the lake is raised over 46 ft. As the surface of the lake is not less than 23 square miles, nearly 900,000,000 cubic meters can be retained. The minimum flow in the river is in this way increased from 5-47 cubic meters per second, or the water power at Rjukan only from 30,000 to 250,000 H. P.

To give you some idea of the development of our industry I let pass in review the factories we have had at the different times:

Dates.	Factories.	H. P. utilized.	Em- ployes.	Work- men.
July 1903	Frognerkilens Fabrik.....	25	2	2
Oct. 1903	Anterlokken	150	1	10
Sept. 1904	Vasmoen and Arendal....	1,000	6	20
May 1905	Notodden	2,500	1	35
May 1907	Notodden and Svaelfos..	42,500	12	103
Nov. 1911	Notodden, Svaelfos, Lien- fos and Rjukan I.....	200,000	143	1,340

According to the results of the use of our nitrate of lime, it is stated that it is the same as the Chili salt-peter and for certain soils it is even better. I have the pleasure of telling you that we today are sending many thousands of tons of the Norgersalpeter to California and Hawaii to be applied to the fruit orchards and sugar plantations; and the demand is twice as large as last year.

That our nitric acid and nitrate of ammonia are enjoying a good reputation is shown by the following extract from an English periodical, "*The Sphere*." It was a peculiar coincidence that just on my trip over here I happened to see this paper and the article in question. There it reads—"Nitric acid is the main constituent of guncotton, dynamite and smokeless powders. One of the chemicals made at Notodden greatly reduces the heat of discharge, thereby prolonging the life of a big gun," and further:—"Nitrate of ammonia obtained at Notodden by the marvelous electric process described here, is the principal constituent of many of the explosives for mines and is, therefore, of high importance to the navy." I could not wish anything better to be said in favor of our products; you would believe I had put it into the newspaper myself.

If you ask me what above all has contributed to such a rapid development of our industry, then I wish to mention the confidence the financial people gave and the good collaboration between engineers and myself. We all were filled with the same thought, to create something great and useful for our country, and we all had in view the great importance this new industry would have from an international point of view.

There is, however, one thing which I wish to tell you and which more than anything else has contributed to the great success attained in the development of this industry, and that is that I mainly have employed young men for this work. This assertion may appear strange but, I assure you that it is the "lack" of experience which has created this industry. If I had paid attention to all the doubt and hesitation brought forward by the so-called authorities during the

development of our enterprise, the Norwegian people today would never have their nitrate industry. Thanks to the young people, to their undaunted courage, energy and love of action the work has been done, and it is in grateful remembrance of all our struggles in joy and sorrow, that I look backward to the work that has been done and the good results we have obtained today. The Norwegian nitrate industry is not alone a technical but also a financial success, and I have been able to keep my promise to the big financial institutions, the Banque de Paris and the Société Générale, and also to our German associates, who today all are proud of the assistance and confidence they gave to the industry.

My own country, the small Norway, who is the youngest daughter of the family of the electrical industries, does no more need to be proud alone of the discovery of the South Pole, but is glad to be able to contribute her share in the solution of the most important questions relating to the world's household.

THE PERMANENT FIREPROOFING OF COTTON GOODS.*

By WILLIAM HENRY PERKIN.

The problem of the prevention of fire has always been one of the most pressing and at the same time one of the most difficult and perplexing with which mankind has had to deal. It is said that the Romans attempted to render wood fireproof by dipping it in a bath made of vinegar and powdered clay.

This treatment, so strongly reminiscent of processes employed many years afterward, would no doubt be effective in rendering the wood less liable to inflame, but it can hardly have had wide application, because vinegar in those days was not easily obtained in quantity and was consequently an expensive substance. I have made a search in a number of old books with the object of discovering some other of the actual methods used in early times in connection with fireproofing, and the first pamphlet on the subject which I have been able to find dates from 1638, when Nikolas Sabbatini published a remarkable paper in which he discussed the need of reform in the administration and construction of the theaters in Italy, and pointed out the danger, which is always present, of fire breaking out on the stage, not only owing to the inflammable nature of the wood employed in the construction of the theater and for the decorations and scenery, but also on account of the inflammability of the cotton material used in the scenery and for the dresses of the players.

He recommends, as a safeguard, that the color used in painting the theater and scenery should be mixed with clay and gypsum, but says nothing about the fireproofing of the dresses.

At a considerable later date—in 1735—Wild suggested a mixture of alum, borax and sulphuric acid for

*From a lecture delivered before the Eighth International Congress of Applied Chemistry.

the same purpose, and in 1740 Fagot, in a paper read before the Academy in Stockholm, recommended a mixture of alum and green vitriol, whereas in the *Dictionnaire de l'Industrie*, published in the year 1786, there is a paragraph in which it is stated that a mixture of alum, green vitriol and salt is effective in making wood and other material fireproof.

After the disastrous fire in Munich on the 14th of January, 1823, which completely destroyed the Hof and National Theater, a large number of experiments were made, with the result that the wood used in the construction of the roof and other parts of the new theater was painted with several coats of sodium silicate and chalk.

A coating of this kind lasts for many years and, although it does not render the wood absolutely non-inflammable, it has at least this value that the incipient fire, which as a rule begins in quite a small way, meets with resistance at the outset, progresses but slowly and is easily extinguished.

At a somewhat later date it was discovered that wood saturated with other salts, such as, for example, copper sulphate or ammonium phosphate, acquires the property of resisting flame; but of all the salts, zinc chloride seems to be the most efficient for this purpose.

In the first place, zinc chloride has great affinity for, and, therefore, attaches itself readily to, woody fiber, and fibers of all kinds and materials saturated with a solution of this salt and then dried are practically non-inflammable. This salt has also this valuable property that it is a powerful antiseptic and therefore very suitable for fireproofing the wood used in the construction of hospitals and other public institutions of a similar nature.

Many disastrous accidents are on record which have been brought about by clothing catching fire; sometimes it is the case of a child whose garments have come in contact with a spark or lighted match, and sometimes disasters of much greater magnitude have resulted from the ignition of costumes made of tow or other inflammable material on the occasion of charity entertainments or fancy dress balls.

It has long been recognized that impregnation with certain salts very much reduces, and, indeed, may entirely destroy the liability of cotton goods to inflame, and of these fireproofing agents I may perhaps be allowed to refer to a few only of the better known and more efficient. If a garment, after washing in the ordinary way, is rinsed in a solution containing alum, or is starched with a starch containing a proportion of alum, the material, after drying, shows a marked reluctance to ignite; but this treatment has many drawbacks. In the first place it makes the material very dusty, and, secondly, the fireproofing is only of a temporary nature, since it is at once removed by contact with water, and the process must therefore be repeated every time the goods are washed. Another solution which has been strongly recommended for the same purpose is made up with three parts of ammonium

phosphate, two parts of ammonium chloride and one part of ammonium sulphate in about 40 parts of water. If the material after washing is impregnated with this solution and dried, or if it is starched with starch made with the solution instead of with water, the dry material only ignites with difficulty, and, as it does not dust and is not prejudicially affected in any other way, this process has been used with advantage not only in connection with wearing material, but also for the fireproofing of lace curtains and other inflammable decorations. But in this case also the fireproofing agents employed are all soluble in water, and one washing is sufficient to remove them entirely, leaving the goods at least as inflammable as before. The process must therefore be repeated every time the goods are washed, and this means expense which, in the long run, becomes considerable.

But a much more serious drawback, to processes of this kind is the trouble they entail, since, in order to fireproof the garment the washerwoman must have alongside the ordinary washtub a second tub containing the fireproofing solution, and this complication, added to the expense of the salts, has been shown to be so serious that processes of this kind are quite impracticable, especially in the homes of the poor. Again, unless the materials or garments after washing have been dried before immersion in the fireproofing solution, this solution cannot be kept uniform, since each garment, being wet when put in, leaves the solution weaker than before and therefore of less protective value. To dry each garment between the washing and the fireproofing entails so much trouble and labor and expense that it would obviously prevent any general adoption of the practice. Although the substances I have mentioned, and the salts of ammonium in particular, possess in a high degree the property of rendering material fireproof, there is one substance which confers the property of resisting fire to cotton goods in such a remarkable degree that it has long attracted attention and must be specially mentioned, and that is sodium tungstate.

A piece of muslin soaked in a weak solution of sodium tungstate and then dried is practically non-inflammable, but unfortunately this salt is again so excessively soluble in water that a mere rinsing in clean water is sufficient to remove it completely and the fireproofing is lost. And this applies not only to sodium tungstate, but also to all the other salts which have, from time to time, been recommended for fireproofing purposes; the result is not permanent, because the proofing is at once removed when the goods are washed in the ordinary way.

The problem on which I was engaged for several years and which has now been successfully solved, in a very simple manner, was that of attempting to discover some process which not only made the goods non-inflammable but also *permanently* non-inflammable, and the researches on this subject were originally started in connection with flannelette, a material very

largely and widely used for clothing, especially by the poorer classes, and one of the most, if not the most, inflammable of all cotton goods.

Flannelette may be briefly described as a kind of calico, the surface of one or both sides of which has been "carded" or "raised" into a nap, the result being that the surface of the calico becomes covered with a fluff of minute fibres somewhat resembling a thin layer of cotton wool. This effect is produced by subjecting the surface of the calico to the action of a series of revolving rollers covered with a vast number of small pieces of sharp steel wire, which tear up the surface, and the material is passed over these rollers over and over again until the required amount of nap has been raised. The result of this superficial covering of nap is—as everybody who has handled flannelette will know—a warm, pleasant and cosy feel, and this is no doubt due to a covering of air being imprisoned by the minute fibres, thus producing a layer which acts as a non-conductor much in the same way as flannel.

Flannelette is indeed little, if at all, inferior to flannel as a non-conducting material, and as it is very cheap and does not shrink in the wash, it has become very popular and is manufactured in enormous quantities and almost universally used for the clothing of children, especially in the homes of the poorer classes.

But it was not long before its increasing use showed unmistakably that it has one terrible drawback,—the nap, which is its peculiar feature, makes it highly inflammable and much more so than the calico from which it was manufactured.

A fireproofing process to be successful must in the first place not damage the feel or durability of the cloth or cause it to go damp, as so many chemicals do, and it must not make it dusty. It must not affect the colors or the design woven into the cloth or dyed or printed upon it; nothing (such as arsenic antimony, or lead), of a poisonous nature or in any way deleterious to the skin, may be used and the fireproofing must be permanent, that is to say it must not be removed even in the case of a garment which may possibly be washed fifty times or more. Furthermore, in order that it may have a wide application, the process must be cheap. What was really to be aimed at was to treat the flannelette in such a way that it acquired practically the properties of wool, which for all ordinary purposes may be taken as the standard of a safe material. Apart from the other conditions which I have laid down, when one considers the vigor with which the ordinary washerwoman scrubs garments with soap, not infrequently with the assistance of the scrubbing brush, and takes into account the wonderful mechanical appliances now so largely used for washing clothes with the least expenditure of time, it will not be thought surprising that the discovery of a process of fireproofing sufficiently permanent to resist all these conditions seemed at first to be almost an impossibility.

Obviously the substance which is to fulfill these conditions must, in the first place, be insoluble in water, and secondly, in order that it is not liable to be re-

moved by mechanical rubbing and does not render the cloth dusty, it must be fixed in the fibre and not be merely on the surface. I have already explained that when calico is dipped in a dilute solution of sodium tungstate, and then dried, the material possesses in a remarkable degree the property of resisting flame, and then again alum has often been recommended for the same purpose. Now when solutions of sodium tungstate and alum are mixed, an insoluble aluminum tungstate is produced, and it is clear that if this insoluble salt could be fixed in the fibre the material would certainly be fireproofed. It furthermore seemed reasonable to suppose that, as the salt is insoluble in water, it would remain in the fibre even after several washings and therefore that permanent fireproofing might be achieved in this manner.

A piece of flannelette was therefore soaked in sodium tungstate, and after passing through rollers, to remove the excess of the solution, left for a considerable time in a solution of alum. It was then squeezed, dried and was passed through the same process again, with the result that the material became almost as fire resistant as asbestos. When, however, the piece was thoroughly washed with soap and water, it was most disappointing to find that the greater part of the fireproofing was removed during the first washing, and after several washings the material was little better than the original flannelette.

While this unexpected result was being investigated, it was noticed that aluminum tungstate is soluble in acetic acid and is reprecipitated when the acetic acid is removed by evaporation or by the action of steam, and as the precipitate formed seemed granular in appearance, it was thought that this process, if applied to the flannelette, might yield a better result than the process of double decomposition had done. Accordingly, a solution was made up of sodium tungstate, aluminum sulphate and enough acetic acid to dissolve the precipitate, the flannelette was thoroughly soaked in this solution, dried and then placed in an ordinary steamer and subject to the action of steam until the odor of acetic acid could no longer be detected.

The material was, of course, non-inflammable, and when it was washed it was found that this property was distinctly more resistant to soap and water than was the case in the first experiment, but after several vigorous washings almost every trace of the fireproofing had disappeared. These negative results seemed therefore to indicate that aluminum tungstate was not suitable for the purpose of permanent fireproofing. On the other hand, the failure of this salt was possibly due to some peculiarities in its specific properties and was not considered valid evidence that other insoluble tungstates might not combine more completely with the fibre and thus resist removal by washing.

A careful examination of the tungstate was therefore made, and such insoluble salts only selected for experiment which, like aluminum tungstate, are colorless, since it is obvious that a fireproofing agent to be of any use must be capable of application to white cloth without staining it. Several hundred pieces of flan-

nelette were treated under the most varied conditions, with all sorts of combinations which it was known would precipitate insoluble tungstates in the fibre, but in no case was a satisfactory result achieved.

However, a fact was noticed which afterwards proved to be of value, and it was this that, of all the salts, the tungstates of zinc and tin seemed to offer the most resistance to washing with soap and water. Thus, when the material had been thoroughly saturated with a solution made up of sodium tungstate, zinc sulphate and enough acetic acid to prevent the precipitation of the zinc tungstate, and the goods after drying were thoroughly steamed, the fireproofing was certainly fixed to some extent, since it required several washings before the material burned at all freely. But no amount of variation of the conditions produced a really good result, and this combination had therefore to be abandoned. Since the tungstate proved to be unsuitable to the exacting conditions of the problem, a general examination of almost every variety of salt, including ferrocyanides, aluminates, arseniates, antimonates, zincates and plumbates was made. Many of these could not be employed in connection with wearing apparel in any case, because of their poisonous nature, but it was thought that this general examination, which lasted several months, might yield some indication of the type of salt likely to prove resistant to soap and water, if, indeed, such type of salt existed at all. And as a matter of fact these experiments did prove to be most valuable, because when the results were all tabulated the generalization gradually became apparent that certain soluble salts, such as aluminates, antimonates, zincates, and plumbates, in which the oxide of the metal functions as an acid, yielded precipitates especially with zinc and tin salts which exhibited much greater resistance to washing than the commoner insoluble salts, such as barium sulphate or magnesium phosphate. This generalization ultimately led to a very careful examination of the dissolves in alkalis to form stannites and stannates, salts of tin, because, as is well known, the oxides of tin and tin therefore belongs to the class of salts just mentioned, and it very soon became evident that these salts do actually possess the power of combining with the fibre to a greater extent than any of the salts which had previously been experimented with.

In one experiment it was noted that a piece of flannelette, which had first been saturated with a solution of sodium stannate and dried, and afterwards similarly treated with a solution of zinc chloride, was quite non-inflammable. After the sample had been subjected to a vigorous washing with soap and water a considerable amount of the fireproofing still remained, because when a light was applied to the cloth it only ignited with difficulty, burned very slowly, and either went out of itself or was easily extinguished on shaking the material.

This development was so promising that the experiment was repeated in a great variety of ways, but although several results were obtained which were much

better than anything which had been seen before, it was disappointing to find that in all the cases the greater part of the fireproofing was lost after repeated washings.

In a later series of experiments the first solution was again sodium stannate, and the second consisted of sodium tungstate, zinc acetate and sufficient acetic acid to prevent precipitation of the zinc tungstate formed. The result in this case was so good, the material being practically as safe as wool, even after repeated washings, that the first commercial permanently fireproofed flannelette which was placed on the market was made on these lines.

It was soon found, however, that the material thus treated had two serious drawbacks; it had a tendency to go damp, and an unpleasant smell of acetic acid remained even though the material had been steamed and washed, after the fireproofing process, before being sent out. And apart from these two faults, the fireproofing was still not sufficiently permanent and the cost of the process was too great for it to be considered a satisfactory one.

A further series of careful comparative tests seemed to indicate that the undoubted advance which had been made was mainly due to the use of the stannate, and it was therefore decided to carry out a series of experiments using salts of tin exclusively.

The fabric after being treated with sodium stannate as before, was, in the earlier of these experiments, passed through a fixing bath containing stannous chloride. A very permanent fireproofing was again obtained, but the stannous chloride, being a reducing agent, tended to destroy or affect the colors of the material, and the process would, therefore, be generally applicable only to white cloth.

In order to get over this difficulty stannic chloride was employed, instead of the stannous salt, as the fixing agent, and to avoid any tendering of the material care was taken that the stannic chloride solution should be of such a strength that a little stannate was left unchanged in the material.

An excellent fireproofing was again obtained, for not only did the material show very little tendency to inflame, after it had been washed several times with soap and water, but it had also in such other respects as appearance and feel almost ideal properties, the only objectionable feature being a slight tendency to dust on rubbing and shaking. Now in this particular experiment, in which sodium stannate and stannic chloride had been employed together, the substance which must have been produced in the fibre, and to which the fireproofing must therefore have been due, is stannic oxide, and it seemed clear that this oxide or its hydrate must have some remarkable power of combining with, or attaching itself to, the fibre which enables it to resist removal by washing and rubbing.

But this process still left something to be desired on the score of economy. A certain amount of the tin was undoubtedly wasted, for, in addition to that lost through a portion of the stannate being left unfixed,

it was noticed that a considerable amount of the tin oxide, which was formed by the action of the alkali of the stannate on the stannic chloride, was not permanently fixed in the fibres of the material, and was therefore removed during the subsequent washing. Tin is so expensive that, in a process to be commercially successful, this loss must obviously be avoided.

There are many ways in which stannic oxide may be precipitated from sodium stannate, and one of these, commonly used in ordinary analytical chemistry, consists in adding certain soluble salts such as sodium sulphate or ammonium nitrate to the solution of the stannate, when the whole of the tin is precipitated as oxide or hydrate. In order to find out whether some process of this kind would precipitate this oxide in such a condition that it would remain permanently fixed in the fibre, a number of pieces of flannelette were soaked in sodium stannate and, after thoroughly drying, separately passed through various solutions containing sodium or ammonium salts at the ordinary temperature and at temperatures up to the boiling point. Although, as was to be expected, the results were not uniformly good, a certain degree of permanent fireproofing was always achieved, and consequently the matter was systematically followed up, with the result that a process was gradually evolved which yielded material possessing quite remarkable properties. The process is briefly this:

The flannelette (or other material) is run through a solution of sodium stannate, having a density of approximately forty-five degrees Tw. in such a manner that it becomes thoroughly impregnated. It is then squeezed to remove the excess of the solution, passed over heated copper drums in order to thoroughly dry it, after which it is run through a solution of ammonium sulphate having a density of about fifteen degrees Tw. and again squeezed and dried.

Apart from the precipitated stannic oxide, the material now contains sodium sulphate, and this is removed by passage through water; the material is then dried and subjected to the ordinary processes of finishing. A long series of trials, carried out under the most stringent conditions, have conclusively proved that material subjected to this process is permanently fireproofed. No amount of washing with hot water and soap will remove the fireproofing agent; or in other words, the property of resisting flame lasts so long as the material itself lasts. This extraordinary property of resisting soap and water seems to me to indicate that the oxide of tin is not present merely as an insoluble precipitate in the cloth, but must have entered into some actual combination with the fibre, yielding a compound which is not broken down by the action of the weak alkali of the soap. But a matter of hardly less importance from the practical point of view is that the material is not only permanently fireproofed by the process I have just described, but it also retains and acquires properties which make it as perfect a material in all other respects as could be desired. In the first place the treatment has no effect on

the delicate colors which are now so generally employed in connection with the manufacture of flannelette and other cotton goods, and very careful experiments have demonstrated the fact that the insoluble tin compound in the fibre has not the slightest deleterious action on the most delicate skin. In addition, the presence of the tin compound in the pores gives the cloth a softer and fuller feel than that of the original flannelette, and what perhaps is the most unexpected result is the fact that the material is considerably strengthened by the process.

A series of tests made by the Manchester Chamber of Commerce proved that the tensile strength of flannelette is increased nearly twenty per cent as the result of the introduction of the tin compound into the fibre.

Further and very exhaustive tests made at the Municipal School of Technology, Manchester, on a machine specially designed for testing the wearing properties of fabrics, showed an even greater gain in durability in the case of the fireproofed flannelette. These separate and independent tests conclusively showed that the increase in strength and durability was approximately equal to the cost of the fireproofing treatment, so that garments made from the permanently fireproofed flannelette are as a matter of fact no dearer than those made from ordinary flannelette and are at the same time as safe as if made from flannel.

This permanently fireproofed flannelette is now manufactured on the large scale by Messrs. Whipp Bros. and Tod in Manchester, under the name of "Non-Flam," and although its introduction has been slow, it is being increasingly used and will, in all probability, ultimately entirely replace the ordinary inflammable variety. One of the difficulties experienced in connection with its general introduction is the fact that, owing to the high price of tin, which is now quoted at about \$1.050 per ton, the cost of the process is not inconsiderable but, even with tin at this high price, the extra cost is not more than 2 cents per yard or about 3 to 4 cents for a child's garment.

It is hardly necessary for me to say that this process can be applied to any cotton fabric and is especially valuable in connection with muslin, because this material is so often used, especially on the stage, for dresses which, on account of their flimsy nature, are naturally highly inflammable. Another direction in which the process may be used with great advantage is in connection with lace curtains. Many disastrous fires have occurred by reason of the ignition of lace curtains, and there can be no doubt that the greater majority of these would have been avoided if the curtains had been treated by the "Non-Flam" process.

It seems to me that it is obvious that, if this process or some other process capable of giving the same protection from fire, were adopted in the case of all inflammable cotton goods and especially in the case of material used for garments, many disastrous fires and the appalling loss of life, especially among young children, might be avoided.

METALLURGY.

THE WEST PROCESS FOR SINTERING FLUE DUST.*

By JAMES G. WEST.†

Before the days of Mesaba ore discoveries the blast furnace people were not troubled to any extent with the blowing over from the furnace top of quantities of very fine particles of iron-bearing materials, or flue dust. They had a comparatively loose, easy burden to work. The hard high-iron ores of 20 or more years ago gave them very little trouble in regard to this loss, now becoming greater as the percentage of the Mesaba ores increase in furnace burdens. Data gathered over a good many years show that the Mesaba ores themselves are becoming finer in texture. In those days very little was heard regarding slips, or hanging, or sudden loosening of the hot mass of material in the furnace, causing large quantities of very fine dust to be thrown out with the issuing gases. We did not hear of clean gas for the hot blast stoves and boilers; high heats were easily obtained on the comparatively clean surface of the brick checker work.

In those operations the losses of iron ores charged into the furnace were not given very much thought, owing to their smallness. But the growing scarcity of these hard ores is compelling the use of more and more Mesaba ore until at present there are plants that are using all Mesaba in their burdens. To appreciate what this means to the furnace manager Table I of sieve tests shows how fine this mixture is becoming.

TABLE I.
Group No. 1

Per cent remaining on sieve:		Through							
2.	8.	20.	40.	60.	80.	100.	100.		
27.50	26.69	15.19	10.72	4.81	3.19	1.84	10.06		
26.00	28.53	16.56	9.44	3.91	2.75	1.66	11.15		
31.22	25.09	14.12	9.06	3.69	2.47	1.44	12.91		
Ave. . .	28.24	26.77	15.29	9.74	4.13	2.80	1.64	11.37	
Group No. 2.									
25.87	20.87	9.27	9.92	8.24	4.27	2.84	18.72		
29.06	19.82	8.05	9.52	14.78	.95	1.16	16.66		
21.59	21.69	9.98	11.86	9.05	5.30	3.87	16.66		
Ave. . .	25.50	20.76	9.10	10.43	10.69	3.50	2.62	17.34	
Group No. 3.									
29.24	23.99	11.75	10.87	6.62	3.28	2.59	11.66		
29.53	28.26	12.96	7.69	6.17	1.56	2.80	11.03		
27.19	27.35	11.95	11.45	5.04	2.54	1.40	13.08		
Ave. . .	28.65	26.53	12.22	10.00	5.94	2.46	2.26	11.92	
Group No. 4.									
35.34	32.53	12.50	4.63	2.03	1.63	.84	10.50		
32.33	32.62	14.80	10.89	7.02	2.02	1.53	7.79		
34.44	22.40	14.78	9.85	5.43	2.09	1.90	9.11		
Ave. . .	34.04	26.18	42.08	8.46	4.83	1.91	1.42	9.13	
Group No. 5.									
25.58	23.77	12.24	12.05	9.03	3.03	2.00	13.30		
32.22	22.38	9.26	11.26	8.37	2.25	2.00	12.26		
23.88	22.97	12.34	11.38	8.00	3.84	3.28	14.31		
Ave. . .	27.23	23.04	11.28	11.56	8.47	3.04	2.43	13.29	

Besides the "group ores" there are a great many

others that run just as fine, some as high as 24 per cent, through the 100-mesh sieve.

The gas pressures on a blast furnace top may vary within very wide limits. There are some plants that will average 7 to 11 in. of water; others may go as high as 30 in. of water. Combined with pressure we have the up-rushing gases coming out of the mass at the stock line with great velocity and meeting the down-falling stock from the bell. A great deal of the material above shown will be caught and carried along by the momentum imparted by the gases. This dust, a great deal of which is that passing through the 20-mesh sieve, as the tables above will show, is caught in receivers or settles along the gas flues. Some of the finest may be carried over to the hot blast stoves and boilers, depositing in these places and reducing the heat absorption of the apparatus. It is a difficult matter to get entirely rid of this dust in the gases, and it is a rule that as long as there is motion in the gases some of the dust will be carried along. To get rid of this fine dust in these gases there have been developed a large number of scrubbers, washers, cleaners, etc.

PRODUCTION OF FLUE DUST COMPUTED.

To enable one to get an insight into this waste we will make use of some data extending over a period of eight years. These show that with blast furnaces using about 70 per cent Mesaba ore and working under normal conditions, the dust is equal to 4 per cent of the total materials charged. This includes ore, stone and coke. The average requirement of ore per ton of metal will be about 1.9 tons, that of coke 2,240 lb., and of limestone 1,000 lb. Using these figures, we will construct the following table, estimating the production of flue dust in the year 1911:

	Tons.
Pig iron production of the furnaces using Mesaba ore	= 22,000,000
Tons ore used (22,000,000 × 1.9)	= 41,800,000
Tons stone (22,000,000 × 1,000/2,240)	= 9,821,000
Tons coke (22,000,000 × 1,000/2,240)	= 22,000,000

Total 73,621,000
Average production of dust, 4 per cent. = 2,945,000

This can be placed at still a higher figure, for not over 90 per cent of the total loss goes into the above percentage. Of the dust coming over with the gases, 85 per cent is caught in the large gas receivers at the furnaces and this is the material which will be spoken of at all times in this paper.

Sieve tests of flue dust taken over a period of two years, all coarse coke being taken out before the test, showed the following:

Per cent remaining on sieve:		Through							
2.	8.	20.	40.	60.	80.	100.	100.		
0.65	1.2	7.02	17.37	31.53	7.93	5.49	28.29		

*From The Iron Age.

†Assistant superintendent of blast furnaces, Edgar Thomson Works, Carnegie Steel Co.

This test cannot be taken as a standard, because a great deal depends upon the regularity of the furnace operation, wind blown and nature of the ores used. Also some plants are screening the coke used, thus removing a large part of the breeze before the coke is charged into the furnace. Other plants are wetting their burdens very heavily. This also tends to reduce the quantity and also affects the quality of the dust. The softness of the coke used also has a great deal to do with the quantity produced, a soft coke increasing the amount to a very considerable extent. The figures in Table II represent sieve tests of dust from a blast furnace that was rolling or slipping:

TABLE II.

Per cent remaining on sieve:								Through
2.	8.	20.	40.	60.	80.	100.	100.	
24.60	6.60	10.60	13.62	15.08	6.17	4.10	19.23	
19.03	2.83	11.70	17.86	20.17	5.18	3.58	14.95	
12.79	.51	4.88	8.84	28.20	10.00	6.79	27.49	

As a rule the part of the dust that passes through the 20-mesh sieve is the most valuable, containing most of the iron ore. That part remaining upon the 20-mesh sieve is mostly stone, coke and pieces of ore low in iron and rather high in silica. For future use it pays to screen the dust through the 20-mesh sieve, if it is to be treated to increase the size of the individual grains or masses.

CHEMICAL PROPERTIES OF FLUE DUST.

These may vary as widely as do the sieve tests, but Table III is a good illustration of the dust, taking off all material remaining upon a 20-mesh sieve and from a blast furnace using 75 per cent Mesaba ore in the burden. All fine coke dust was screened out before charging the coke into the furnace.

TABLE III.—ANALYSIS OF FLUE DUST.

	SiO ₂	Fe.	Mn.	P.	Mois.	Al ₂ O ₃	CaO.	MgO.	C.	CO ₂	S.
1	5.20	48.52	.39	.050	15.4	1.6	1.29	.30	4.71	.28	
2	5.49	43.31	.43	.032	16.6	1.5	1.33	.31	8.41	.10	
3	6.99	48.56	.43	.038	14.8	2.2	1.45	.09	4.68	.66	
4	6.36	46.41	.46	.047	15.10	2.43	1.26	.48	3.67	.56	
5	7.76	48.97	.38	.036	13.35	2.39	1.16	.42	3.73	.81	
6	9.58	47.09	.31	.035	13.65	2.05	.99	.27	3.75	.83	
7	9.23	46.60	.48	.034	14.15	2.18	1.67	.31	4.48	1.00	.10
8	8.26	46.69	.70	.037	16.10	2.25	1.30	.34	3.04	.70	.12
9	7.22	48.03	.44	.034	14.45	1.65	1.41	.25	2.57	.88	.10
10	9.46	47.16	.37	.036	14.80	1.97	.85	.28	2.50	.57	.07
11	9.23	46.43	.43	.034	11.80	2.07	1.37	.37	5.28	.83	.063
12	6.99	46.30	.47	.034	12.65	2.59	1.83	.45	7.41	1.60	.064

If a blast furnace is slipping or rolling heavily the total carbon in the dust may run up as high as 16 to 20 per cent. The carbon contents of the dust play an important part in the treatment, either by heat or by mechanical operations, which is employed to put it into various forms for recharging into the blast furnace. Most of the impurities, silica, etc., are combined mechanically with the iron; separation by screening does not produce any great degree of concentration. This also applies to the flue coke dust, the percentage remaining very nearly the same in all sieves under 20 mesh.

PHYSICAL PROPERTIES—A POOR HEAT CONDUCTOR.

The structure is mostly in the form of grains that seem to allow large quantities of air or water to be absorbed by any mass into which it may be shaped. It will hold approximately 25 per cent of water by weight

without separation. It approaches sand in its resistance to compression, remaining granular after subjection to enormous pressures. Experiments have been made where 25,000 lb. per sq. in. has been used and upon taking from the mold, the heavy pressure having caused cast iron to be disturbed or swelled out, the dust mass itself would crumble easily under the touch. Any slight fall would shatter it into small pieces. It is a very poor conductor of heat; a very slight layer will act as an insulator.

In a study of the heat conductivity of flue dust particles it is noticed that the rate of fusion does not exceed 1 in. an hour, and if the gases do not come in contact with all surfaces of the mass the unexposed surface will not be heated thoroughly. The heat penetration or conduction may be increased in both rapidity and extent by subjecting the mass to a high degree of pressure before application of the heat. This is explained by the fact that pressure excludes the contained air and brings the particles of the ore closer together and in this condition they conduct heat more rapidly.

Experiments make it self-evident that all particles of the material in masses must be subjected to the same degree of heat if the melting mass is to be uniformly cemented together. We cannot depend upon conduction to aid to any quick operation.

Cementation starts very close to 2,300° F. Any temperature below this point only serves to change some of the other physical properties of the dust. Temperatures above this produce close fusion or liquefaction. The degree of latitude between semi-fusion and liquefaction is very slight. This is aggravated to a considerable extent if carbon be present. If too much carbon is present it tends to retard the fusion, until it is consumed by the heat; and if the mass is withdrawn before the coke or carbon is consumed, there will be no fusion of the ore particles, the resulting mass being very grainy in structure.

MAGNETIC PROPERTIES.

The magnetic properties vary a great deal in the different kinds of dust and depend on the temperature of the furnace top from which they were produced. About 60 per cent of the total iron, as shown in the chemical analyses in the foregoing tables, will be magnetic. By exposing to heat at varying temperatures it has been demonstrated by repeated tests that this percentage may be raised.

TABLE IV.—PER CENT OF MAGNETIC MATERIAL IN FLUE DUST AT VARYING DEGREES OF HEAT.

	Temp. F.	SiO ₂	Fe.	Al ₂ O ₃	CaO.	MgO.	Loss.	Ign. Car-	Per et.
								bon.	Orig.
Mag.	75°	4.04	63.65	2.81	.20	.10	None	1.80	68.80
Non-mag.		11.26	36.95	1.85	2.26	.10	25.65	20.55	31.20
Mag.	200°	5.71	59.45	2.18	.51	.10	3.61	2.70	72.85
Non-mag.		11.18	35.80	3.00	2.75	.36	26.86	14.10	27.15
Mag.	400°	4.02	62.60	2.27	.18	.60	.79	2.00	73.85
Non-mag.		10.01	36.25	2.86	2.24	.10	26.21	22.20	26.15
Mag.	500°	3.89	62.85	2.08	.13	.32	None	1.90	78.80
Non-mag.		9.88	41.50	2.90	1.79	.10	20.73	48.30	21.20

By continual heating for some time at a temperature

about 1,500 lbs. about 84 per cent of the total iron in ordinary flue dust can be rendered magnetic.

The impurities in the dust may be eliminated by magnetic separation, either by the wet or dry methods, or by specific gravity. Either of the first two methods will recover only about 60 per cent of the iron in the original dust, for as shown before all the iron present may not be in the form of magnetics. In Table V is given the performance of a magnetic separator on blast furnace flue dust, the iron and carbon percentages being shown for both magnetic and non-magnetic portions. Six different lots of flue dust are represented in the table.

TABLE V.

		Magnetic portion		Non-magnetic portion	
		Iron.	Carbon.	Iron.	Carbon.
		Per cent.	Per cent.	Per cent.	Per cent.
No. 1		60.83	3.23	33.87	27.08
No. 2		59.51	4.21	43.74	16.40
No. 3		64.15	2.15	43.59	15.98
No. 4		57.40	6.16	42.43	17.05
No. 5		64.95	2.75	48.58	10.70
No. 6		63.70	3.99	45.91	12.70

For briquetting by pressure and heat, lower carbon content is desired. The specific gravity method consists of passing the dry dust over a shaking porous bottom, air being forced upward. This makes the lighter pieces of iron-bearing material and the coke dust rise to the top, where it is taken off by raffles to the side, the heavier material going one way and the lighter stuff in another direction. For this class of work this method gives decidedly better results. All the iron may be recovered if desired, or if a high iron content in concentrates is desired a small portion of iron will have to be sacrificed. In briquetting by pressure and heat the rule has been to combine these two methods, taking all the magnetics out that is possible, and then passing what remains over the specific gravity machines.

TABLE VI. WORK OF SPECIFIC GRAVITY MACHINES.

Tailings from			— Specific gravity —						Tailings.		
Magnetic separators.			Concentrates.								
Fe.	C.	CO.	Fe.	C.	CO.	Fe.	C.	CO.	Fe.	C.	CO.
38.30	22.12	1.81	44.60	8.91	2.75	21.4	46.35	1.58			
45.40	11.89	1.38	49.50	9.43	1.65	28.8	31.69	1.89			
37.70	16.25	2.10	47.50	10.65	2.12	25.5	37.95	1.65			
40.60	11.98	1.65	47.20	6.42	2.69	...	...	...			
Avg.	40.50	16.30	1.70	47.00	8.60	2.30	25.2	38.70	1.70		

By this combination of magnetic and specific gravity machines the iron loss for ordinary work may be only 10 per cent. In case a high iron content is desired, the specific gravity machine is far superior on this dust. Where high iron is desired the dust is classified by screening to give the best results, although screening or sizing may not at all times be necessary for obtaining certain desired results. Some of the results with specific gravity machines are shown in the following:

Carbon, per cent.	Iron, per cent.
2.66	64.05
3.62	61.52
4.92	60.42
3.45	62.03
2.72	62.84
2.49	62.53
1.51	63.04

Further adjustments in this specific gravity machine have produced even lower carbon contents.

There have been numerous attempts to use flue dust in a raw state. The majority of furnacemen would express a negative voice if they were to be asked the advisability of its use. A notable exception to this rule is the practice of the Ohio Works of the Steel Corporation. At this place it has been used for some years and with telling results. The tendency of the times are toward a treatment of some kind whereby the size of individual grains or masses will be increased.

METHODS OF TREATING FLUE DUST.

Numerous methods have been practiced in treating the dust. All these come under the following divisions:

1. Mechanical pressing, with addition of some foreign substance to aid in holding the mass together.
2. By mixing the fuel with the material to be treated, igniting, and forcing air up or down, throwing the mass lying upon a porous bottom.
3. Rotary kiln.
4. Briquetting by pressure and heat.
5. Exposing a large surface of the dust to the action of the flame and addition of fresh material as fast as it will form an agglomeration.

The physical properties by all these methods differ greatly, and the object aimed at should be kept in mind before any one is selected. The considerations are: Methods of handling the product, distance to be transported, whether the product is to be stored or subjected to the action of the elements, etc. A redivision of the process, according to the physical properties of the product would be as follows:

Processes producing lump masses of considerable size:

- No. 1.—General briquetting process.
Processes producing a porous mass:
No. 2.—Greenwalt, Dwight-Lloyd, Brown, Grasselli, etc.

- Process producing small lump masses:
No. 3.—Rotary kilns.
No. 4.—Grondal process.
No. 5.—West sintering method.

All of these methods are in operation with varying output. For the treatment of flue dust, briquettes by heat and pressure are probably producing more tonnage than any of the other methods, and a great many experiments have been made to adapt the apparatus to the peculiarity of the dust.

THE WEST SINTERING APPARATUS

All the processes above named have been before the public for some time, with the exception of the West sintering method, which was patented by the Carnegie Steel Co. in behalf of the writer, and which was the logical outcome of the production of lump masses for the blast furnaces as well as the open hearth, at the same time reducing the preliminary treatment of the dust to remove the carbon, by concentration (when it is desired) and pressing, to produce a mass that would have great strength and density, and stand a large

amount of handling and weathering without serious deterioration.

The invention consists of a furnace with a movable bottom, on which a block of the material is built as fast as the continuous action of the heat will agglomerate or stick the particles together. The material can be delivered to the furnace in several ways:

1. Letting it fall from the roof and spreading out mechanically to form a thin layer.
2. Using a kind of injector operated by air, moving it over the area.
3. Using a type of continuous furnace with the bottom moving slowly along, the dust being charged in definite places.

By all these methods we get a very thin layer of material subjected to heat, which softens it before another quantity is added. In any of these methods the charging may be so timed as to make the addition of the dust almost continuous. By the West method crude dust can be handled without regard to its pecu-



Fig. 1.

liarities, and a very desirable product obtained. It does not require pressing, concentrating, etc., as in other processes, to produce lump masses. After the block or mass is built up to the capacity of the furnace it is withdrawn and the sinter removed by means of a crane; it is then broken to sizes that may be desirable. If this breaking is done while the mass is red hot there will be a minimum of effort and cost.

CONSTRUCTION OF THE FURNACE.

In Fig. 1 the construction of the furnace used in the West sintering method is shown. The flue dust is charged in a fine stream through an opening in the roof of the furnace, and is so highly heated that the particles of ore form a thoroughly sintered layer immediately upon reaching the hearth. In falling the finely divided solids are brought into intimate contact with the gases. The furnace consists of a roof and sides, with a longitudinal vault or passage through which the trucks carrying the movable hearths may pass. The sides of the furnace are equipped with burners, *A*. Passages *B* in one side of the furnace connect with the stack. Extending vertically through the roof is the opening *C*. The hearth *D* is made of suitable refractory material, supported upon the truck *E*. Each furnace is provided with several such trucks with the hearth prepared ready to be pushed into the furnace vault.

In operation, a layer of fine ore or flue dust is laid upon the hearth, to a depth sufficiently thick to insure that the ore will not stick to the refractory bottom, the

thickness of this layer being sufficient to prevent it being entirely heated to a plastic state. The furnace bottom is further prepared by building a wall *F* along the marginal edges of the top surface of the hearth. Refractory clay or brick are employed for this purpose. When the hearth has thus been prepared it is moved into the vault of the furnace and curtain doors are lowered to cover both ends of the vault. The burners at the side of the furnace are then lighted and the furnace hearth or bottom is heated to the desired temperature, after which the sintering operation is begun.

CHEMICAL AND PHYSICAL CHARACTERISTICS.

Below are given results of analyses of flue dust and of West sinter, also the percentages of various sizes of the original material and the percentages of three sizes of the resulting sinter:

Analyses of Crude Dust and Sinter.					
Crude Dust.		Per cent—	Sinter.		Per cent—
Silica	8.77	13.50	Silica	9.60	8.50
Iron	47.19	49.50	Iron	64.20	66.20
Phosphorus	0.032		Manganese		0.56
Manganese	0.38		Phosphorus		0.049
Moisture	12.75		MgO		3.36
CaO	2.16		MgO		0.54
MgO	1.79		CaO		0.51
Carbon	10.20		Sulphur		0.12
Sulphur	0.05		FeO		
			FeO		
			Carbon		0.41

Percentages of Dust on Sieves, with Size of Sinter.

	2.	8.	20.	40.	60.	80.	100.	100.
Before treatment	65	1.2	7.02	17.37	31.53	7.93	5.49	28.79
	Per cent. Per cent. Per cent.							
	1/2 in. 2-m. 3-in.							
After treatment and unloaded at								
furnace bins		1		5		94		

In cases where it was desired to make as large lumps as possible, we have some of the following figures:

8x6x7 in.	64 lbs. net
8x6x2 in.	= 12 lbs. net
7x4x3 in.	= 13 lbs. net
8x5x3 in.	= 16 lbs. net
6x7x2 1/2 in.	= 13 lbs. net
7x5x4 in.	= 16 lbs. net
7x5x3 in.	= 14 lbs. net
7x5x2 1/2 in.	= 11 lbs. net
7x5x2 in.	11 lbs. net

The iron in these lumps averaged 65 per cent. As the operation is under complete control at all times, the resulting product may be either dense or porous; but at all times there will be a great deal of strength. The table below shows the properties of product made from flue dust by heat and pressure, and that produced by the West method:

	Heat and pressure	Sinter.
	Per cent.	Per cent.
Absorption	15.0	6.9
Porosity	37.0	18.9
Specific gravity	3.9	3.2
Apparent specific gravity	2.7	2.6

The chemical content of the product from this process, compared with that of some of the others, may be seen from the following table, crude dust being used at all times:

	Heat and pressure.			—West sinter—		Rotary Porous kiln. product.	
Iron	61.4	61.7	60.9	65.7	64.2	66.2	58.07
Silica	9.0	8.2	9.2	9.7	9.6	8.5	10.68
							11.3

EXPERIENCE WITH SINTER—COST OF PLANT.

Under this method of production we have a superior type of apparatus, in which the heat degree can be kept practically constant and even, over the whole surface of the mass, very little dependence being put upon conduction to do the work. This is very important, as was shown under the description of the physical properties of the dust. It is necessary regardless of the form of apparatus to have the heat distributed as widely as possible through the mass to be sintered. The product of the furnace shown has been used on blast furnaces with good results, and did not seem to in any way disturb the regular method of operating. As high as 30 per cent of the total ore burden has been withdrawn and an equal amount of sinter substituted without any derangement of required results.

With the growing scarcity of low silica, high iron ores for open hearth use it is becoming recognized that a substitute must be found. To this end the dust is concentrated, pressed and sintered into lump form. The tests using lump masses have given excellent results. Dense sinters from the pits have also given good results. The estimated cost to operate the various forms of briquetting and sintering apparatus is as follows:

Fuel	\$0.05 (a)	\$0.39 (c)	\$0.35 (c)	\$0.25 (c)
Labor operation....				
Labor repairs.....	.45	.61	1.25	.25
Material				
All other costs.....				
Total	\$0.50 (d)	\$1.00	\$1.60	\$0.50

(a) Gasoline cost for igniting fuel.

(b) Metallurgical and Chemical Engineering for September.

(c) Coal at \$2 per ton (12,000 B.t.u. per lb.).

The cost of installing per ton day of 24 hr. in large plants is as follows:

Porous product	\$150
Rotary kiln	300
Heat and pressure.....	400
West	100

If in proximity to natural gas or crude oil the last-named figure could be reduced to \$80. Where blast furnace gases could be used the cost of the last three would be considerably reduced.

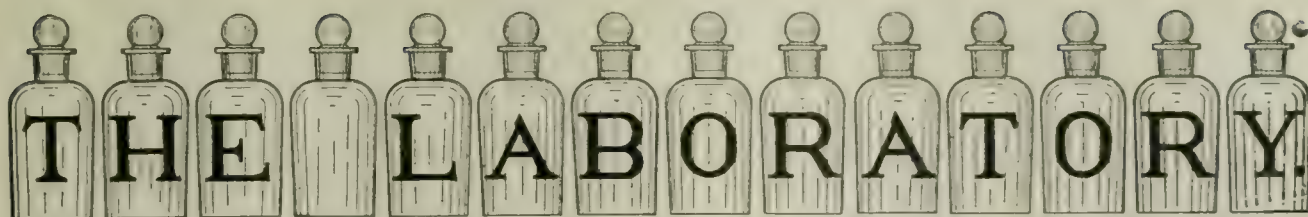
The General Syndicate, or Federation of French Cotton Spinners, whose headquarters are at 9 Rue St. Fiacre, Paris, has established at Havre a laboratory for determining the percentage of moisture or any abnormal degree of dryness that may exist in cotton. The establishment of this laboratory, which began operations on Sept. 20, 1912, was in pursuance of the recommendation of the last International Cotton Congress, held at Barcelona, Spain. The method of operation, according to a U. S. Consular report, is as follows: Samples are taken by employees of the laboratory in the presence of buyer and seller (or their representatives), each of whom selects five bales out of every 100. Three samples are taken from each of the 10 bales indicated, thus making 30 samples. The samples are placed in metallic boxes, which are

hermetically closed, removed to the laboratory, weighed with great precision, their weight noted on a card form, and then placed, for three hours, in a ventilated oven kept at a temperature of 95° C. (203° F.), where the cotton is almost completely dried. From this they are taken to another ventilated oven kept at a temperature of 115° C. (239° F.), where, without being removed, they are weighed every 10 minutes, note being taken of the change. When weight ceases to be lost, the cotton is considered to be absolutely dry, having given off all its moisture. The difference between the weight of cotton in this condition and its weight when taken from the bail—allowance being made for the normal degree of 8½ per cent of moisture—represents the excess of moisture contained in it on its arrival. That is to say, assuming that 100 lbs. of cotton should weigh in its normal condition 108½ lbs., and that this cotton, when dried by the process referred to, weighs exactly 100 lbs., its condition may be considered as perfect. Any variation would represent either an excess of dryness or moisture. In the event of excessive moisture being discovered, the spinner to whom the cotton is sold would make a claim against either the shipper in the United States or his agent at Havre for the loss sustained, claiming the actual value of the staple after allowance has been made for weight represented by excessive moisture. The ovens and apparatus constituting the plant at Havre were manufactured by Leroy, Bigot & Co. of Roubaix, France. They are adapted for accurate and speedy work.

A new theory for the prevention of dust explosions was discovered by Dr. J. Harger in a paper read last February before the Liverpool (England) section of the Society of Chemical Industry. The plan, in brief, is to prevent the ignition of coal dust, and, in a measure, the ignition of firedamp, by reducing the amount of oxygen in the air currents flowing through the mine. Dr. Harger stated that while a lamp would not burn in air in which the oxygen had been reduced to 17 per cent, a man could do continuous hard work in such an atmosphere and not notice that it differed from ordinary air containing 21 per cent oxygen. He also stated that a man would not notice or feel any bad effect until the oxygen was reduced to below 14 per cent. At 12 per cent the shortage was noticeable, and a danger point was reached when the percentage of oxygen in the air was reduced to 7½ per cent.

The production of hydrated lime in the United States in 1911 was 304,593 short tons, valued at \$1,372,057, an average price of \$4.50 a ton, as compared with 320,819 short tons, valued at \$1,288,789, or an average price of \$4.02 a ton in 1910.

Metallic filament lamps exported from Germany during the first seven months of 1912 numbered 20,000,000, valued at \$6,000,000.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

The Analysis of Iron and Steel—(Continued).

THE DETERMINATION OF PHOSPHORUS.

—The most convenient method for the determination of phosphorus in iron and steel is by the so-called "acid-alkali" titration of the yellow precipitate of ammonium phosphomolybdate. The principles of this method, together with directions for the preparation and standardization of the solutions of sodium hydroxide and nitric acid, are given in full detail in a former paper of this series (this journal, Vol. XV, No. V), wherein the analysis of iron ore is discussed. On this account only the special applications of the method to pig iron and steel analysis need be given here.

Solutions.—The solution of NaOH should be of tenth normal (N/10) strength, or thereabouts, and the HNO₃ solution should be made exactly equivalent to it. (Such solutions will contain respectively about 4 gr. NaOH and 6.5 c.c. of HNO₃ sp. gr. 1.42, per litre.) The phosphorus standard of the alkali solution is determined by titrating the "yellow precipitate" obtained from samples of standard iron or steel, the procedure throughout being the same as that used in the analysis of the samples.

The Analysis.—Samples of two grams weight are weighed into 500 c.c. Erlenmeyer flasks and dissolved in 75 c.c. of nitric acid of sp. gr. 1.13 (1 conc. HNO₃: 3 of H₂O) by the aid of heat. In order to oxidize the combined carbon, 15 c.c. of KMnO₄ solution (5 gms. per litre) are added and the solution again boiled. The operation of oxidation is complete when the pink color of the KMnO₄ has disappeared and given place to the brown precipitate of MnO₂. At this point sulphurous acid solution is added in slight excess and the whole heated until the precipitate dissolves. The solution, which should be clear, is allowed to cool, and then 13 c.c. of ammonia solution sp. gr. 0.90 are added slowly, the contents of the flask whirled until all of the ferric hydroxide dissolves, heated (or cooled) to 85° C., and finally 50 c.c. of the ammonium molybdate solution added. The flask is immediately stoppered, wrapped in a towel and shaken continuously for five minutes. The precipitate of phosphomolybdate is filtered promptly, washed five times with 1% nitric acid and then five times with 1% potassium nitrate solution. The precipitate, freed from iron and from acid, is then dropped, with its paper, into the original flask and over

it is run from the burette about 40 c.c. of standard NaOH solution, three drops of phenolphthalein added and the excess of alkali immediately titrated with the standard acid.

For the standard:

$$\frac{\text{Wt. of sample} \times \% \text{ of P}}{\text{No. of c.c. of Sol.}} = \text{Wt. P per c.c. NaOH sol.}$$

No. of c.c. of Sol.

In the analysis:

$$\frac{\text{No. c.c. of NaOH} \times \text{Standard}}{\text{Wt. of sample}} \times 100 = \% \text{ P}$$

THE DETERMINATION OF CARBON.—Since carbon exists in cast iron in the free condition as graphite and in the combined condition as carbides, it is necessary to know not only the total percentage of carbon, but to know also the division of this total into the two forms in which the carbon is present. Steel, on the other hand contains its carbon in the combined condition only, so one determination of total carbon is required. This single determination should be of a high order of accuracy.

Graphite in Iron.—One gram samples are weighed into small beakers. If the material is white iron, the samples are dissolved in 100 c.c. of hydrochloric acid solution, sp. gr. 1.12; if foundry or Bessemer iron, 100 c.c. of dilute nitric acid, sp. gr. 1.20 are used. In either case, after solution is complete a few drops of hydrofluoric acid are added and the whole boiled thoroughly.

The residue, consisting of carbon and some hydrocarbons, is then filtered off on a Gooch crucible where it is washed free from acid with hot water. The carbon compounds are then removed by repeated washing with 5 per cent ammonia solution until the washings are colorless. Finally all ammonia is washed out with water and the residue dried at 95° C. to constant weight. The carbon is then burned off by ignition at the temperature of the blast lamp and the crucible cooled and re-weighed. The loss in weight represents the weight of graphite, from which the percentage is calculated.

The Determination of Total Carbon in Iron or Steel.

—This determination depends upon the combustion of the total carbon content of the material to carbon dioxide and the subsequent absorption of the carbon dioxide in caustic potash solution where it is weighed. There are several methods whereby this may be accomplished: The entire sample of metal may be burned direct in oxygen, the carbon dioxide being caught and

weighed. The fused silica combustion tube lends itself admirably to this method.

The carbon may be separated from all other constituents by solution of the material in cupric potassium chloride, and then burned, either in the standard form of combustion furnace or in the Sheimer crucible.

The following method yields excellent results.

The 3-gram sample is weighed into a 400 c.c. beaker and there treated with 150 to 180 c.c. of copper potassium chloride solution. The solution is prepared as follows: 400 gms. of pure $\text{CuCl}_2 \cdot 2\text{KCl}$ are dissolved in a liter of distilled water and the solution filtered, after which 200 c.c. of concentrated hydrochloric acid are added. To the sample, 10 c.c. concentrated hydrochloric acid are added and the whole warmed to 60°C . and stirred continuously by means of a mechanical stirrer until first all of the iron and then all of the precipitated copper is completely dissolved. This will require several hours. The residue which contains all of the carbon is then filtered on an asbestos felt and washed first with a little dilute HCl and then with water until free of acid. The felt with the residue of carbon is then removed from the crucible to a watch glass, all particles of carbon being wiped from the sides of the crucible by the aid of bits of asbestos. The entire precipitate of carbon with the asbestos is then dried at 105°C .

The dried precipitate is then transferred to a platinum (or porcelain) boat, which is placed in the tube of a combustion furnace. The end of the combustion tube beyond the boat being hot when the boat was introduced, the boat is heated as rapidly as the tube will allow and then oxygen is turned through the apparatus. The combustion should be complete in 30 minutes after the oxygen was turned on and the boat came to full heat. At the end of this time the heat is gradually turned off and the oxygen replaced by air. The air should pass through the train at least 20 minutes to insure the complete sweeping out of the CO_2 and replacement of the oxygen. The Geissler tube is then allowed to stand in the balance case for half an hour and weighed. The grain in weight is CO_2 .

Wt. CO_2 times 0.2727

— — — — — 100 — % C.

Wt. of sample

Preparation of the Combustion Train.—A Jena glass tube of $\frac{1}{2}$ in. bore is provided with a plug of asbestos at a point about 6 in. from one end. Granular copper oxide is poured into the tube for a distance of about 18 in., and another asbestos plug inserted. The tube is then placed in the combustion furnace. A gasometer full of oxygen and a source of air (either another gasometer or the tap from a laboratory supply) are connected by means of a "Y" tube with a series of wash bottles containing (1) a concentrated solution of KOH , (2) concentrated H_2SO_4 , (3) dry soda-lime. The last of these bottles is connected with

the combustion tube by means of a short rubber tube and a well fitting rubber stopper carrying a glass tube. The further end of the combustion tube is similarly fitted with a stopper, and through the single hole the side tube of a calcium chloride U tube is passed. The calcium chloride used in this tube must be completely saturated with CO_2 previous to use. This is done by passing the CO_2 from a Kipp generator through the tube for half an hour, and then removing the excess CO_2 by passing air for another half hour. It is well to treat a considerable quantity of calcium chloride in this way and preserve it for use in combustion work. To the drying tube is attached a Geissler tube containing a 50 per cent solution of KOH . The drying tube attached to the KOH bulb and weighed with it is filled as follows: A small plug of cotton is placed at the bottom. On this is poured soda lime to a point half day to the end. On the soda lime is placed calcium chloride, and finally another cotton plug. The tube is then closed with its stopper carrying a short glass tube. The train is now prepared. Before the run it is necessary to get it completely dry. To do this, light the burners of the furnace, turning them very low until the tube is thoroughly warmed, and then gradually raising the heat until the entire tube within the furnace is at a dull red heat, allowing air to pass through the entire train during the time of heating and for some time after the tube has reached its maximum temperature. Now the heat is cut down gradually until all burners are turned off except those under the middle portion of the copper oxide, the Geissler tube is detached and, after standing half an hour in the balance case, is weighed and returned to its place in the train and air run through. All is now ready for the combustion of the sample.

When not in use the tube should be kept closed by stoppers or otherwise as the copper oxide is somewhat hygroscopic. A much better control of the flow of gas is possible if a large aspirator bottle is attached to the Geissler tube, a drying tube being placed between. The flow should be such that the bubbles of oxygen or air can be readily counted as they pass through the Geissler tube. The small drying tube which is a part of the KOH bulb should be renewed for at least every two determinations. The writer renews it for each run. The KOH will last for a good many determinations.

Good determinations of carbon by combustion require careful manipulation and considerable mechanical skill. Unless one is constantly making such determinations the results should always be duplicated.

Colorimetric Determination of Combined Carbon.—When a sample of iron or steel is treated with dilute nitric acid under the proper conditions, a yellow color is developed which is due to, and its depth a function of, a part of the combined carbon. Since this color is not a function of all of the combined carbon it is

necessary that the sample of known carbon content which is used as the standard be of a nature similar to the samples for analysis, and that samples and standard should have undergone the same heat treatment. Thus mild steel can only be compared with mild steel standard, gray iron with gray iron, etc.

Having the proper standards of known content of combined carbon, the determination is carried out as follows:

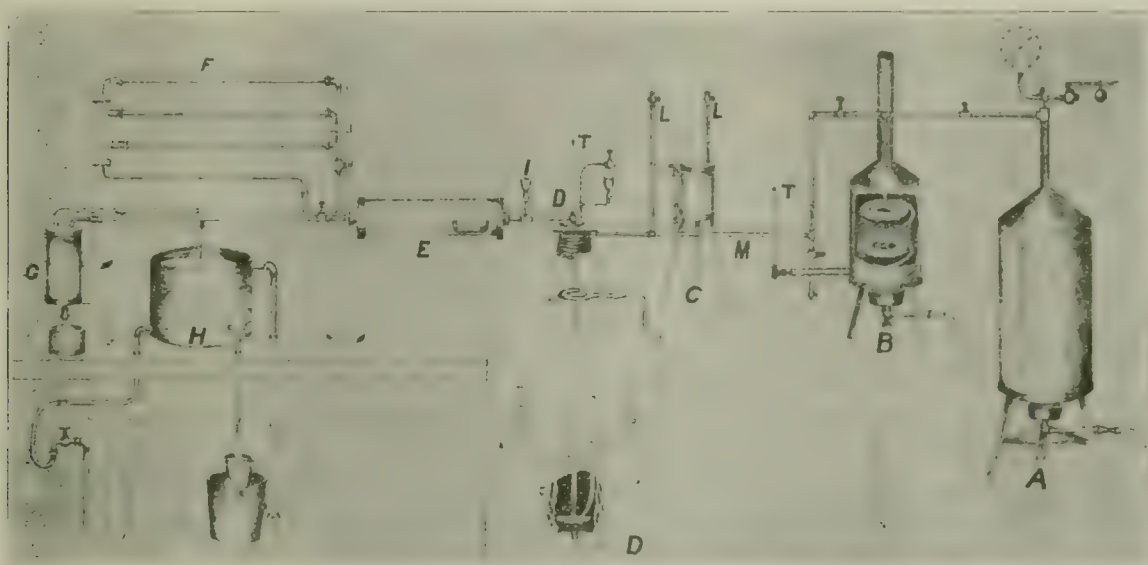
Samples of standard and unknown of exactly 0.2 gm. are weighed into test tubes 6 ins. by $\frac{5}{8}$ in. The tubes should be clean and perfectly dry. They are placed in a rack that supports them upright in a water bath filled with cold water, and to each is added 7 c.c. of nitric acid sp. gr. 1.2, measured accurately. A very small funnel is placed in the top of each tube to act as

APPARATUS FOR THE EXAMINATION AND STUDY OF THE BEHAVIOR OF VALVE AND CYLINDER OILS AND OTHER PETROLEUM LUBRICATING OILS IN SATURATED AND SUPERHEATED STEAM, CARBON DIOXIDE, AIR AND OTHER GASES.*

By P. H. CONRADSON.†

The introduction of a high degree of superheated steam in locomotive and stationary engine practice has brought about the necessity of adding tests to the ones usually made of cylinder oils, whether straight petroleum stock, or mixture of the same with smaller or larger amounts of saponifiable fats.

The writer has constructed and used an apparatus for some time in the investigation of cylinder oils suit-



Apparatus for Examination of Valve and Cylinder Oils.

a condenser, and the water in the bath is brought to a boil and boiled until all carbonaceous matter is dissolved, the tubes being removed and shaken from time to time. When solution is complete the rack is lifted out of the water bath and placed in a dish of cool water. The solutions so prepared should be exposed as little to the light as possible.

The colors are compared in the following manner: Pour the solution of the standard into the comparison tube, rinsing the test tube carefully, and making the bulk at least 15 c.c. Treat the sample in the same way and compare the colors. Dilute the darker of the two until it exactly matches the lighter, adding cold water cautiously. When the colors in the two tubes are the same, the percentages of combined carbon are in direct proportion to the volumes of the solutions, all other conditions being the same in each case.

Vol. for Standard : Vol. for sample :: % in Standard : x

x :: % combined carbon in sample.

able for the lubrication of valves and cylinders in connection with the use of highly superheated steam in locomotive service.

The apparatus is essentially as shown in the cut.

A, small steam boiler with gas, steam gauges and pipe conditions.

B, superheater with armored thermometer, T, and steam connections (a small circulating water heater with double copper coils answers very well).

C, sight-feed lubricator with connections.

D, steam vessel (a conical cast iron retort for distilling mercury, about 95 mm. deep and about 75 mm. in diameter at top, provided with two strong screw clamps to keep the lid tight, answers very well) surrounded on the outside, as indicated, by a coil of copper pipe, 5-6 mm. inside diameter, for further heating of the steam and gases used in the tests; this coil is tapped into the bottom of the steam vessel containing

*Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.
†Chief Chemist, Galena Signal Oil Co., Franklin, Pa.

a suitably supported dish of about 25 cc. capacity (an ointment box about 55 mm. in diameter, 18-20 mm. high), into which the oil to be examined is fed drop by drop from the sight feed lubricator C (or a given amount of oil is poured into the cup I). Through the lid is inserted an armored thermometer, T, reaching down into the dish. The steam vessel thus arranged and connected is surrounded and covered by a suitable asbestos hood.

L, pipe connections for the gases used.

E, heavy glass cylinder, about 200 mm. long and 18-20 mm. inside diameter, containing a small rectangular boat or dish; beyond E is a glass tubing system, F, connected up, as shown, with brass fittings; each glass tube is about 500 mm. long and 8-9 mm. inside diameter; at the further end is attached a steam separator and oil collecting vessel, G, consisting of an

The temperature in D is maintained for a given length of time at or near 400° F., noting if any oil vapors are coming over; by shutting and opening the steam valve it is easy to see if any vapors are coming over with the steam.

The temperature is increased in increments of 25°-50° F. at a time, until the desired temperature is reached, noting the behavior of the oil vapors passing on with the steam through the glass pipe system, etc. It is interesting to note that cylinder oils containing rather a large percentage of saponifiable fats or fat oils generally come over at much lower temperatures than the main portions of the petroleum stock oils that are commonly used in compounding first-class cylinder oils.

In further study of the behavior of oils, the boat in the glass cylinder E may be filled through the cup I to

TABLE I.—COMPARATIVE TESTS OF SAMPLES OF CYLINDER OILS.

	A.	B.	C.	D.	E.	F.
Flash point (open cup).....	545° F.	550° F.	605° F.	595° F.	550° F.	365° F.
Burning point.....	610° F.	630° F.	695° F.	680° F.	630° F.	415° F.
Gravity at 60° F. Baumé.....	26.4	26.1	24.7	25.9	...	33.5
Sp. gr. at 15° C.....	0.895	0.897	0.905	0.898	...	0.856
Color.....	Light	Dark	Dark	Very dark	...	Yellow
Gas, test before fire test.....	Good	Good	0.5 cc.	4.0 cc.	...	...
Gas, test after fire test.....	Good	Good	Good	3.0 cc.	...	...
Cold test flows.....	+55° F.	+32° F.	+45° F.	+34° F.	+30° F.	Zero
Saponifiable fats.....	Trace	Trace	Trace	Trace	15 per cent	None
Vis. Saybolt at 212° F. (60 cc.).....	133 sec.	146 sec.	215 sec.	216 sec.	...	...
Barbey Ixomet 500° F. (180 units=30 cc.).....	45 sec.	51 sec.	61 sec.	60 sec.	...	...
Hot air test at 540° F. (loss)...	15 per cent	11 per cent	2.5 per cent	5.5 per cent	...	...
Gas, test after.....	Good	Good	0.5 cc.	3.5 cc.	...	...
Carbon test residue.....	2.15 per cent	2.70 per cent	4.90 per cent	5.10 per cent	...	...
SO ₂ in residue.....	0.023 per cent	0.03 per cent	0.03 per cent	0.04 per cent	...	...
Loss in superheated steam at—						
400° F.....	0.0 per cent	0.0 per cent	0.0 per cent	0.0 per cent	0.0 per cent	32 per cent
500° F.....	5.0 per cent	4.0 per cent	1.5 per cent	1.0 per cent	5.0 per cent	67.1 per cent
600° F.....	18.5 per cent	18.0 per cent	6.5 per cent	8.5 per cent	21.5 per cent	...
700° F.....	44.0 per cent	34.0 per cent	32.5 per cent	40.5 per cent	...	...
Total loss up to 700° F.....	67.5 per cent	56.5 per cent	40.5 per cent	50.0 per cent	26.5 per cent	99.0 per cent
Gas test of oil:						
Residue from 700° test...	Good	Good	1.5 cc.	3.0 cc.	...	...

ordinary glass chimney fitted up with brass caps; to this, condenser H is connected by means of copper tubing.

In this apparatus any desired temperature may be maintained, at least up to 1,000° F.; this is 300°-400° higher than is required under the most exacting service conditions, as far as superheated steam temperature is concerned.

In studying the behavior of valve and cylinder oils in an atmosphere of superheated steam, the steam is passed from the small steam boiler through the superheater B and into the steam vessel D, through its pipe coil (lamp being lit under D) and out through E, F, G and H.

When the temperature reaches and is regulated in D to 400° F., oil is fed drop by drop from sight feed lubricator C (or the cup I is filled); the steam is shut off and the valve in C (or I) opened, letting the oil run into the dish in D; the steam valve is then very gradually and carefully opened so as to let through any desired amount of steam.

the left, and subjected at various temperatures to slow currents of superheated steam, carbon dioxide and air, or mixtures of the same. The glass cylinder E during the last test is surrounded by a heavy asbestos covering to prevent radiation.

The cylinder oils may leave a residue in the dish in D at steam temperatures below 700° F.; if so, such residue should give a clear solution in 90 cc. of 0.65 sp. gr. (87° B.) petroleum ether (Pennsylvania) and show no precipitate on standing. At steam temperatures of 850°-900° F., all the oil has usually volatilized with the steam; good oils should leave no carbonaceous or coky residue.

While this apparatus was designed principally for the study and behavior of valve and cylinder oils in atmospheres of steam at various temperatures, it can be adapted very readily for the study of other oils at various temperatures in currents of air, carbon dioxide or other gases or mixtures of same with and without steam.

The accompanying table shows comparative tests of

five samples of cylinder oils, A, B, C, D, E and F, a petroleum distillate of interest in connection with the study of cylinder oils in superheated steam:

Hot Air Test = 13 grams oil in shallow, round, flat-bottom iron dishes, exposed six hours at 540° F. in a specially designed air bath.

Gasoline Test = 10 cc. oil, 90 cc. petroleum ether 0.65 sp. gr. (from Pennsylvania crude), in graduated flat precipitating tubes, taking reading after 1 hour's standing.

Carbon Test using 35 grams oil, according to Conradson's apparatus and method.

Superheated Steam Test = 13 grams of oil used.

Sample "A" in a superheated steam test at 800° F. (427° C.) left no residue. Sample "C" left 2.5 per cent dry carbonaceous residue.

Sample "E," containing 15 per cent of saponifiable fats, subjected to the superheated steam test, lost 26.5 per cent up to 600° F.; the oil residue from this test contained 17.5 per cent saponifiable fats; this indicates that the petroleum oil stock ("B" used) goes off with the steam somewhat faster in proportion to the fat oil up to 600° F. (350° C.).

The steam pressures used in these tests were about ten to twelve pounds per sq. in. A large volume of superheated steam passed through the apparatus during the tests (about 40 cc. condensed steam per minute).

In these superheated steam evaporating tests about 13 grams of oil were weighed into the small dish placed inside the steam vessel D. (The capacity of the small iron dish is 50 cc., having a diameter of about 48 mm. and 30 mm. high, with flat bottom.)

The steam vessel with the oil in the dish was heated up to about 350° F. (176° C.), passing a slow current of natural gas through the apparatus, then superheated steam was admitted, the gas shut off, and the temperature raised up to the required degree and kept constant for about 75 minutes; the volatile matter in the oils at the given test temperature generally were carried over with the steam inside of 60 minutes, allowing about 15 minutes' extra steaming. At the end of each given temperature test, the steam and heat were shut off; after cooling, the dish containing the oil was weighed and replaced in the steam vessel, and the operation repeated for the next temperature test.

The mineral production of New Zealand for 1911 was, according to the Government report, as follows: Gold, 455,266 oz.; coal, 2,068,073 tons; kauri gum, 7,587 tons; silver, 1,311,043 oz.; all other minerals, £22,200. Of the last figure, it is understood that over one-half was due to scheelite exports. Outside of the kauri-gum diggers it is estimated 7,400 persons were employed in metalliferous mines and 4,200 in coal mines during the year.

A Pennsylvania silk manufacturer is considering establishing a silk mill at Honolulu.

THE VOLATILE ACIDITY OF GUM TRAGACANTH COMPARED WITH THAT OF INDIAN GUM.*

By W. O. EMERY.†

The primary object of this investigation was to devise additional methods for the detection of Indian gum when substituted for or in admixture with tragacanth. A study of the literature early led to the conviction that among the degradation products of these gums there must be one susceptible of quantitative isolation and sufficiency characteristic to serve as an indicator of the purity, and therefore of the quantity, of parent substance involved in its hydrolysis. Such an indicator was believed to be represented by acetic acid, already isolated from one Indian gum and reported as being present in another. The hope was entertained that tragacanth under like treatment might fail to yield this acid, but as will presently appear, experiment proved otherwise.

As defined by the United States Pharmacopœia, tragacanth is the "gummy exudation from *Astragalus gummifer* Labillardière, or from other species of *Astragalus*, family Leguminosæ, appearing in ribbon-shaped bands varying in size and from 1 to 3 mm. thick, or in irregular pieces of the same, long and linear, straight or spirally twisted; externally whitish, marked by more or less pronounced longitudinal or eccentric lines or ridges; translucent, fracture, short, tough, rendered more easily pulverizable by a heat of 50° C. (122° F.)."

While it is possible that the products known to the trade as "Indian gum" and employed so extensively in this country may vary as to their origin, it appears reasonably certain that two gums at least are justly characterized by this term, namely those of *Sterculia urens* and *Cochlospermum gossypium*, both of which find local application as substitutes for tragacanth. It is equally certain that none of the so-called Indian gum has its origin in any species of *Astragalus*. Most of the Indian gum reaching this country bears little or no resemblance to tragacanth. A careful comparison of the commodity with authentic samples obtained direct, both from London and from India, clearly indicates that it corresponds in all essential points to the gum of *Sterculia urens*. It occurs in irregular, striated, sometimes twisted, translucent, or transparent lumps, never in ribbon-shaped bands or leaves.

In view of such physical characteristics, successful adulteration or substitution of whole gum tragacanth with Indian gum is no easy matter, and yet the latter product is occasionally offered for sale in the bazaars of India as true tragacanth.¹ It is, however, the powdered form of tragacanth that presents to the sophisticator more alluring possibilities. Owing to its extended use in the arts as well as in medicine, coupled

*From Circular 91 of the Bureau of Chemistry, U. S. Department of Agriculture.

†Chief, Synthetic Products Laboratory, Division of Drugs, U. S. Bureau of Chemistry.

¹Zörnig, *Arzneidrogen*, 1909, p. 654.

with a relatively high price for the better grades, adulteration with the cheaper Indian gum has within the past few years been of frequent occurrence, hence any method looking to the detection and estimation of such adulterant must be welcome to all desirous of obtaining pure powdered tragacanth.

CHEMICAL PROPERTIES OF GUM TRAGACANTH.

According to researches carried on by O'Sullivan² tragacanth consists of starch granules, cellulose—that portion insoluble in boiling water, cold dilute acids, and alkalis—likewise water-soluble gum yielding a series of gum acids of the nature of geddic acid, bassorin, bassoric acid, nitrogenous and mineral matter. As the result of an investigation of tragacanth from various sources, Hilger and Dreyfus,³ among other conclusions, found that this product differs not only as regards chemical constitution, but also with respect to the proportion of degradation products formed when subjected to hydrolysis. None of the investigators of tragacanth, however, has to the writer's knowledge, ever considered the possibility of acetic or other volatile acid constituting one of the hydrolytic products of this gum, due perhaps to the fact that it is odorless and without acid reaction in aqueous suspension, conditions not obtaining in the case of the two Indian gums herein considered. The remarkable property possessed by the gums of *Sterculia urens* and *Cochlospermum gossypium* of developing an acetous odor when exposed to moist air has been commented on by various authors; in fact, an examination by Robinson⁴ of the hydrolytic products obtained with the gum of *Cochlospermum gossypium* developed the fact that an amount of acetic acid was formed equivalent to 14.4 per cent of the original gum.

When gum tragacanth is heated with an aqueous mineral acid, as phosphoric or sulphuric acids, and the products of such action subjected to steam distillation, an acid distillate is obtained from which acetic acid can readily be isolated in the form of its silver salt. The procedure employed is as follows:

Treat 20 grams of whole gum first in the cold with 200 cc. of distilled water and 10 cc. of sirupy phosphoric acid until completely swollen, then subject for several hours to the full heat of the steam bath, whereby the mass gradually becomes partially liquefied, then distil the product with steam and evaporate the distillate to dryness in the presence of barium carbonate. Treat the residue with a little hot water, filter, and distil the filtrate, amounting to about 30 cc. with steam after the addition of 5 cc. of sirupy phosphoric acid.

On treating the distillate with silver oxid and filtering, characteristic plate-like needles are obtained, which on ignition prove to be silver acetate, as is evidenced by the following analytical data; 0.2048 gram of substance gave 0.1321 gram of silver; calculation for $C_2H_3O_2Ag$ gave 64.65 per cent of silver, 64.50 per cent being found.

There can, therefore, be no doubt that acetic acid constitutes one of the degradation products of tragacanth when heated with mineral acids.

ESTIMATION OF ACETIC ACID.

Quantitatively, the acetic acid or, rather, "volatile acidity"⁵ is estimated as follows:

Treat 1 gram of the whole or powdered sample in a 700 cc. round-bottomed flask, provided with a long neck, for several hours in the cold with 100 cc. of distilled water and 5 cc. of sirupy phosphoric acid until the gum is completely swollen. Boil gently two hours in connection with a reflux condenser, whereby a nearly clear, colorless solution is effected. A very small amount of cellulose substance will remain undissolved. Now subject the hydrolyzed product to slow distillation in a vigorous current of steam until the distillate amounts to 600 cc. and the acid residue to about 20 cc. This should not be driven too far, however, otherwise there may be danger of scorching the nonvolatile, organic degradation products, with consequent possible contamination of the distillate. It has been found that a spray trap if used in connection with the flask containing the hydrolyzed gum, is effective in preventing traces of phosphoric acid being carried over into the distillate. Titrate with tenth-normal potassium hydroxid in connection with 10 drops of phenolphthalein solution, finally boiling the liquid under examination until a faint pink color persists. Run a control on same amount of distillate obtained by a parallel operation, with omission of gum, but using like quantities of other ingredients and observing the same conditions as in the test.

With a relatively large number of authentic gums (Turkey, Aleppo, and Persian), both whole and powdered, the following results were obtained:

Results on 35 samples of gum tragacanth lump (cubic centimeters of tenth-normal potassium hydroxid):

3.9, 3.5, 4.2, 4.0, 3.4, 4.0, 3.2, 3.5, 4.0, 3.9, 3.4, 3.4, 3.6, 3.4, 3.5, 4.2, 4.0, 3.6, 3.3, 3.6, 3.8, 3.4, 3.3, 3.6, 3.4, 3.1, 3.3, 3.5, 3.4, 3.7, 3.4, 3.7, 3.7, 3.2, 3.4. These figures represent an average volatile acidity of 3.6 cc. Assuming this acidity to be due solely to acetic acid, it would be equivalent to 2.15 per cent of acetic acid in the original gum.

Results on 21 samples of gum tragacanth powdered (cc. tenth-normal potassium hydroxid): 3.8, 3.5, 3.5, 3.5, 3.6, 4.1, 3.8, 3.4, 3.9, 3.9, 3.5, 3.7, 3.8, 3.9, 3.6, 3.8, 3.6, 3.8, 3.5, 3.6, 3.8. This gives an average volatile acidity of 3.7 cc. equivalent to 2.20 per cent of acetic acid in the original gum.

As regards the acetic acid content of Indian gum (*Cochlospermum gossypium*) it has already been shown by Robinson⁶ to yield 14.4 per cent of this acid. That of *Sterculia urens*, however, though early recorded by Guibourt⁷ as emitting an acetous odor, has never before to the writer's knowledge been examined

²J. Chem. Soc., Trans., 1901, 79: 1164; Proc. 1901, p. 156.

³Ber. d. chem. Ges., 1900, 33: 1190.

⁴J. Chem. Soc., Trans., 1906, 89: 1496.

⁵The term "volatile acidity" as used herein is the number of cubic centimeters of tenth-normal potassium hydroxid required to neutralize the volatile acid or acids obtained, by subjecting the products of the action of aqueous phosphoric acid on 1 gram of gum to distillation with steam.

either as to the identity or the quantity of the acetic acid present. Five grams of Indian gum (*Sterculia urens*) were therefore treated in substantially the same manner as outlined for the isolation of the silver salt from the hydrolytic products of tragacanth. It may not be amiss to note in this connection that while tragacanth yields a practically colorless solution when boiled with aqueous phosphoric acid, Indian gum, on the other hand, gives a pink or rose colored solution, a sure indication of an unknown sample that this product is present. The acid distillate obtained gave with silver oxid characteristic plate-like needles, which on ignition yielded values corresponding to silver acetate: 0.2010 gram of substance gave 0.1300 gram of silver, calculation for $C_2H_3O_2Ag$ gave 64.65 per cent, 64.67 per cent being found.

Gram samples of whole and powdered Indian gum (*Sterculia urens*) were examined for volatile acidity, exactly as in the case of tragacanth, with the following results:

Results on 9 samples of Indian gum, lump (cc. tenth-normal potassium hydroxid): 26.3, 26.1, 26.6, 27.7, 27.1, 28.3, 25.9, 26.1, 26.8. These data indicate an average volatile acidity of 26.7 cc., corresponding to 15.91 per cent of acetic acid in the original gum. The last of the nine samples, yielding 26.8 cc., was an authentic one obtained direct from the Indian Government; this acidity corresponds to 15.97 per cent acetic acid.

Results of 11 samples of Indian gum, powdered (cc. tenth-normal potassium hydroxid): 26.5, 26.3, 26.1, 27.3, 26.3, 26.9, 25.4, 25.6, 27.7, 26.8, 26.6, 25.6, 27.6, 26.0. The average volatile acidity in this case is 26.5 cc., corresponding to 15.79 per cent of acetic acid.

CONCLUSIONS.

From the foregoing data it appears that the volatile acidity or amount of volatile acid developed by gram samples of tragacanth, on the one hand, and Indian gum (*Sterculia urens*), on the other, is fairly constant, sufficiently so, indeed, to serve, in conjunction with other well-known tests, as a very reliable criterion for estimating the purity or quantity of either alone or in admixture. The volatile acidity of Indian gum (*Sterculia urens*) as compared with that of tragacanth is nearly 7.5 times as great.

According to a report of the Peruvian Government the mineral production for 1910 was as follows: Gold, 708 kg.; silver, 252,565 kg.; mercury, 350 kg.; copper, 27,347 metric tons; lead, 1,866; antimony, 49; vanadium ore, 3,130; bismuth, 24; tungsten ore, 12; borax, 2,351; salt, 17,504; coal, 307,320; petroleum, 167,712 tons.

Deposits of carbonate of soda amounting to millions of tons are reported to have been discovered near Pretoria, South Africa.

SCIENTIFIC METHOD IN CELLULOSE INVESTIGATION.*

By C. F. CROSS, B. Sc., F. I. C.

There has recently been published under the title "Die Einwirkung von Wasser und Natronlauge auf Baumwollcellulose" (Berlin, 1912, Borntraeger), an experimental investigation of some of the fundamental constants of cellulose. The author, Dr. M. Robinoff, applies the reactions of cellulose with alkaline cupric oxide in diagnosis of the constitutional variations impressed upon typical celluloses by serially regulated treatments. These reactions, which have been selected and methodized by C. G. Schwalbe in their particular relation to cellulose investigation, are of obvious *à priori* value, and this present investigation is an important confirmation of their diagnostic capabilities.

Thus, to select a convincing case, the author's numbers afford sufficient proof that cellulose is constitutionally modified by contact with highly dilute acetic acid (0.1% $C_2H_4O_2$) at ordinary temperatures, and that by contact with cold tenth normal HCl, as, in the "souring" operations of textile bleaching, there is a progressive modification with the duration of the contact. No other method yet disclosed has been able to diagnose constitutional changes such as these, which are certainly slight, and to Schwalbe, therefore, we owe a contribution of present and potential importance.

Robinoff follows Schwalbe in avoiding theoretical speculative treatment of the subject-matter, and this restraint is no doubt deliberate. On the other hand, the positive purpose underlying this and other investigations of Schwalbe, or inspired by him, is to accumulate quantitative data, and we may refer the reader to our two previous articles to show that our suggestions have been anticipated in this particular direction.

What we also set forth in our suggestions was the view that any set of quantitative data require establishing by convergent verifications. This for the simple reason that cellulose is its own standard. Cellulose requires treatment as a system *sui generis*, and not as a detached individualized molecular unit, comparable in all respects with the general range of carbon compounds. Whether clearly recognized as a postulate or not, investigators are constrained by the exigencies of laboratory experience to work on this basis, and it is implicitly recognized by Robinoff.

All the derivatives of cellulose present themselves in series, with gradations which apparently increase in number with the refinement of method; of these series the limiting cases are the assumed individuals, which are only really individual in the sense of identical ratios of their component residues, which are the common stoichiometrical ratios.

The celluloses themselves present greater difficulty to the investigator than, *e. g.*, their derivative esters, if

*Loc. cit.

†Pharm. J. (London), 1855, 15: 57.

*From the Chemical World.

only for the reason of essential insolubility. Hence the characteristic features of methods applicable to cellulose: quantitative statistics of reactions, and measurements of physical and mechanical properties of the solids, with observations of changes of form and dimension.

In the plan of Robinoff's investigations are included treatments by water at temperatures from 100° to 213°, and by sodium hydrate solutions under an extremely wide range of graduated conditions.

The constitutional effects are measured in terms of hygroscopic moisture and the reactions with alkaline cupric oxide (*a*) of combination, and (*b*) of reduction, and these furnish the desired convergence of correlative effect.

The author's paper must be closely studied by those who have a special, or a *specialist*, interest in cellulose chemistry.

It will interest the general reader to know that in addition to diagnosing such relatively small changes in constitution as result from contact of celluloses with highly dilute acids, the author is also able to show that their constants, and, therefore, constitution, are definitely modified by the papermaker's beating process. The results on this point are worthy of reproduction as they are of importance to a wide range of readers.

A bleached Egyptian cotton, ascertained to be "normal," was employed, and the following numbers are recorded.

Time of beating.	Hygr. moisture.	Copper number.	Cellulose number.	Corrected copper number.	Hydrolysis number.	Corrected hydrolysis number.
0	6.27	0.51	0.29	0.22	3.00	2.44
1	6.60	0.56	0.29	0.27	3.00	2.44
1	7.87	1.07	0.58	0.49	5.12	4.05

As a comment on these results, which are of obvious significance as proof of progressive chemical action, the author adds "they confirm the supposition of certain investigators that in comminuting the fibrous celluloses (true) hydrated modifications of cellulose are produced."

We have maintained this view in accordance with the generalized conclusions from long observation, that cellulose responds to any and every treatment with reagents, however weak, by constitutional change. This has been present to us as the only adequate basis of cellulose technology, and there are current developments of extension and refinement of cellulose processes which are rapidly accumulating definite proofs of the statement. The author's contribution of proof is, however, of greater importance because it is in terms of numbers, and in the particular form of concordant and convergent verifications.

By this investigation several points are established in addition to further proof of the value of these constants of Schwalbe's methods in cellulose investigations.

The author has advanced the conception of the labile constitution of cellulose, and the precise definition of the "normal cellulose."

He has furnished a basis of precise investigation of such important textile processes as involve special purification and preparations of celluloses, more particularly the textile bleaches and "finishes," and the operations of the papermaker.

As a complementary investigation there is now required the extension of the author's observations to such structural forms of cotton cellulose, *e. g.*, yarns and papers, as follow comparison of constants of strength and elasticity.

In 1911 there were 650 producing mines in Italy, of which 352 were sulphur; 88 zinc and lead; coal and oil shale, 35; iron, 31; graphite, 30; salt, 30; asphalt, 15; borax, 12; pyrites, 10; manganese, copper, mercury, oil and gas, 9 each; all others, 11. The outputs of the principal items, arranged in order of descending value, were: Sulphur, crude, 2,682,766 metric tons; zinc ore, 139,719; iron ore, 373,786; lead ore, 38,458; lignite, 553,083; mercury ore, 97,803; asphalt and bitumen, 188,133; iron pyrites, 146,124; petroleum, 10,390; copper ore, 68,136; borax, 2,648; rock salt, 43,763; other salt, 17,251; graphite, 12,621 metric tons; natural gas, 9,021,000 cu. m.; copper pyrites (45% S, 1½% Cu), 19,149 metric tons; mineral waters, 35,320; manganese ore, 3,515 metric tons.

The U. S. Forest Service has recently determined the specific heat of wood for a number of different specimens of twenty of the more important varieties. The results of these studies are embodied in Bulletin 110 of the Forest Products Laboratory Series, written by Frederick Dunlap. From this publication it appears that the mean value for the interval 106°-0°C. was nearly the same for all specimens and all species of oven-dried wood. This average is 0.327, a figure to be compared with the older values 0.467 to 0.650 (Kent's Pocketbook). The variation of specific heat with temperature was also studied and reported to be (above 0°C.) according to the expression $c = 0.266 + 0.00116 t$. Exposure to moisture at high temperature (steaming) gave greatly increased specific heats, but these are not definitely reported on in this publication as further study is planned.

Petroleum exports from Baku for the first half of 1912 are given by the *Petroleum Review*, Sept. 7, 1912, at 3,048,083 metric tons as against 3,040,800 metric tons exported during the corresponding period of 1911.

According to the U. S. Geological Survey the production of domestic tungsten ore in 1911 amounted to 1,139 short tons of concentrates, carrying 60 per cent of tungsten trioxide. In 1910 the production amounted to 1,821 short tons.

ON THE INDICES OF REFRACTION OF CHINA WOOD OIL.*

By LOUIS ELSBERG WISE.

The increasing use of china wood oil in the paint and varnish industries has created the necessity for a proper examination and standardization of this important article of commerce. Much of this drying oil is sent to European and American ports through Hankow, and a rumor is now current that there have been varied attempts to adulterate these shipments with cheaper products, such as soya bean oil. Whether or not these reports are based on fact, the author of this paper is in no position to decide, but he has found it a proper time to review the recent literature, relating to the characteristic properties of the raw material, and to find, if possible, some method by which the purity of the oil could be gauged.

The important characteristics of the oil¹ are its odor, its peculiar drying properties (in which it differs markedly from linseed), its high specific gravity and its coagulation on heating. The saponification, iodine and acid numbers appear to be of little value in judging the oil.

The jelly which is formed on application of heat is elastic and insoluble in the common solvents. It is ordinarily believed that the gelatinization is due to a polymerization; it is undoubtedly *not* caused by oxygen absorption, and it immediately distinguishes wood oil from the other common drying oils.

Several chemists have recently made a study of the physical characteristics of the "go-back" (the varnish maker's name for this coagulation product), and a number of chemical examinations², have been made, which up to the present have led to widely divergent results. A further investigation of the "go-back," as well as the relation between its properties and its technical use, is being made by Mr. Eugene G. Bloch, of our laboratory, and the results of this research may be published at some future date.

Another striking peculiarity of the oil is its high index of refraction. Lewkowitsch states that the refractive index is much higher than that of any other drying oil, and this statement suggested the study of the refractive indices of a number of commercial samples. The data obtained is recorded in the tables given below.

All attempts to get samples of wood oil of known source and purity were without avail. The difficulty was due to the primitive condition in the collection of the oil and its shipment to the coast from the country districts of China. We received a sample from Mr. Bacon (also purchased on the open market) which is supposed to be a standard, but its source has not been indicated.

The results tabulated below, therefore, represent

the refractive indices of *commercial* wood oils shipped to us for use in the manufacture of varnish. The shipments cover a period of approximately eight months, during 1911-1912. Some of them have proved unsatisfactory in the processes of manufacture, and there is some indication that a relation exists between the refractive index and the "working quality" of the oil. That question can be settled only by a far more extended research. Gross adulteration is certainly indicated very clearly and rapidly by the use of the refractometer, and whether foreign oils, present in small quantities may be detected, will depend very largely on the results of future coöperative investigation.

TABLE I.

Mark.	Index of refraction at 25° C.
A.3.20.12	1.5148
A No. 1 A.....	1.5118
A No. 2 A.....	1.5130
A No. 3 A.....	1.5164
A No. 4 A.....	1.5153
A No. 9 A (R. M. S. 3534).....	1.5174
A No. 10 A (R. M. S. 3528).....	1.5174
S. L. J.....	1.5168
Sample from Mr. Bacon.....	1.5186
C $\triangle_{55}$ C	1.5121
C $\triangle_{75}$ C	1.5116
C $\triangle_{83}$ C	1.5167
A No. 19.....	1.5163
R. M. S. 3505.....	1.5099
W. K. C. W. O.....	1.5110

The results in Tables II and III require little comment; they show clearly that the admixture of small amounts of other drying oils lowers the refractive index.

TABLE II.

Sample.	Index of refraction at 25° C.
100 per cent wood oil (mark) A.3.20.12.....	1.5147
95 per cent wood oil, 5 per cent soya bean oil....	1.5122
95 per cent wood oil, 5 per cent linseed oil.....	1.5128
90 per cent wood oil, 10 per cent linseed oil.....	1.5114
100 per cent soya bean oil	1.4751
100 per cent linseed oil.....	1.4810

TABLE III.

Sample.	Index of refraction at 25° C.
100 per cent wood oil (Bacon's sample).....	1.5186
95 per cent wood oil, 5 per cent soya bean oil....	1.5163
95 per cent wood oil, 5 per cent tallow oil.....	1.5161
100 per cent tallow oil.....	1.4833

All indices of refraction were taken *without* the use of water circulation. All refractometric readings were made in the Advanced Physics Laboratory of Columbia University.

In conclusion, I beg to thank Mr. Bloch, chemist for the Standard Varnish Works, for his material aid, Dr. C. C. Trowbridge, of the Department of Physics of Columbia University, for his kind advice and Dr. Parker C. McIlhiney for his just criticism and his help.

*From the Journal of Industrial and Engineering Chemistry.

A MODIFICATION OF THE SWEENEY METHOD FOR CRUDE FIBER.*

By CORNELIA KENNEDY.

The method for the determination of crude fiber as recently modified by M. O. Sweeney¹ does not prove entirely satisfactory for all kinds of feed stuffs, especially those which are rich in protein. In his method an ether extracted sample of feed is first boiled for 30 minutes with 1.25 per cent sulphuric acid. This acid solution is neutralized with 10 per cent sodium hydroxide and 200 cc. of a boiling 2.65 per cent sodium hydroxide solution added and boiled for 30 minutes. The sample is then filtered, washed, dried, weighed, incinerated and reweighed.

The acid dissolves certain nitrogenous bodies, pentosans, gums, etc., and when the alkali solution is added a heavy precipitation of some of these materials is caused. This precipitate is weighed with the crude fiber and consequently materially increases the percentage amount of fiber.

The following modification of the Sweeney method does away with this difficulty, and gives results which check, within the limits of error, with the official method.

As in the above method the prepared sample is first boiled with 200 cc. of a 1.25 per cent sulphuric acid.

thoroughly washed with boiling 1.25 per cent sulphuric acid, which will remove the material precipitated by the addition of the alkali, washed free of acid, removed from the linen filter to a crucible, dried, weighed, incinerated and reweighed.

The Sweeney method has a great advantage over the official method by doing away with a filtration and thus saving time. This advantage is preserved in the modification of the Sweeney method.

Table I shows the results of all three methods on 5 different samples of feeds.

The 1911 mineral output of the Union of South Africa was as follows: Gold, 8,251,240 fine oz.; diamonds, 4,891,999 carats; coal, 7,594,944 tons; copper concentrates and matte (47.46% Cu), 23,098 tons; tin concentrates (67.26% Sn), 3534; lime, 79,389 tons; silver, 896,538 oz.; salt, 40,498 tons; asbestos, 1,266; flint, 2,395 tons. The value of no other single item, excluding certain ceramic products, exceeds £1,500. In December, 1911, there were 10,383 stamps and 259 tube mills at work in the Transvaal, as against 9,800 and 197 for December, 1910. The Transvaal produced 8,249,461 oz. of the total gold output, milling 24,918,648 tons of ore. The Rand produced 7,910,034 oz. of this gold. The silver was all produced either from gold bullion, or from base-metal ores. Of the diamonds, 4,758,307 carats came from mining, and 133,691 from alluvial washing. The Messina Development Co. remains the only copper producer of importance in the Transvaal, concentrating 16,475 tons of ore into 1,856 tons assaying 50.45% Cu. The Cape Copper Co. and Namaqua Copper Co. in Cape Colony are the largest producers of copper, smelting 136,335 tons of ore producing 17,760 tons of 50.21% matte, and also producing 1,058 tons of 30% picked ore and 37 tons of 79% precipitates.

In a letter to the New York Times William S. Myers, official delegate of the Chilean Government to the International Congress of Applied Chemistry, makes the following statement regarding the Chilean nitrate supplies: "First of all, there is a vast amount of unsurveyed nitrate ground on the Chilean pampas that is known to contain immense quantities of nitrate of soda. Second, grounds already surveyed still contain enormous quantities of nitrate. There are probably in round numbers, 1,000,000,000 tons of nitrate in the deposits of Chile, and, without doubt, large supplies also exist on lands now but incompletely prospected. The surveyed and certified tonnage opened up at the present time ready for extracting is fully 250,000,000 tons. The probable life of the surveyed deposits is at least 400 years, even allowing for a steadily increasing annual rate of consumption. Moreover, there remains the interesting question as to whether by the end of the ensuing century we may not find that nature has manufactured an immense additional amount of Chilean nitrate for the uses of the world."

TABLE I.

	Official method.		Sweeney's method.			Sweeney's modified.		
	Per cent.	Average.	Per cent.	Average.	Increase over official method.	Per cent.	Average.	Increase over official method.
Bran	12.04 11.49	11.76	14.21 14.06	14.13	2.37	12.47 12.20	12.33	0.57
Sucreen	0.55		0.15			0.27		
food	14.33		15.92			14.67		
.....	13.92	14.12	15.58	15.75	1.63	14.43	14.55	0.43
Sugar and	0.41		0.34			0.24		
flax feed	6.90		7.44			7.12		
.....	6.89	6.90	7.44	7.44	0.54	7.08	7.10	0.20
Oil meal..	0.01		0.00			0.04		
.....	7.87		10.20			8.81		
.....	7.86	7.87	10.08	10.14	2.27	8.80	8.81	0.03
Bran	0.01		0.12			0.01		
.....	11.37		12.95			11.81		
.....	11.11	11.24	12.94	12.95	1.71	11.69	11.75	0.51
	0.26		0.01			0.12		

Neutralization is done away with, by making the alkali solution of such strength that it both neutralizes the acid and leaves the 400 cc. of 1.25 per cent sodium hydroxide; 200 cc. of a boiling 3.52 per cent sodium hydroxide are therefore added, and the whole boiled 30 minutes. The solution and fiber are then thrown onto a linen filter (which works more rapidly than a gooch because of the nature of the solution) and washed free of alkali. (Suction may be used to cause a more rapid filtration). The fiber is then

*From the Journal of Industrial and Engineering Chemistry.
¹U. S. Dept. Agr., Bur. of Chem., Bull. 137, 157.

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NOTES AND COMMENTS.

German Chemical Works.

According to a writer in the *Revue Generale de Chimie*, the success of the German Chemical Works is not due so much to the value of the chemists, cheap labor and legislation as it is to the marvelous systems of organization. The following are some of the interesting points brought out in the French paper:

The managers of works are usually young men, of an age when the faculties are fully developed. The writer expressed his astonishment at hearing that a manager of 45 years had been pensioned off. "Why not?" was the reply he received. "He has been ten years with the firm, and during that time must have practically applied all his ideas. There would be the risk of his being influenced later by routine and opposing the opinions of younger men. We must make use of the energy of others capable of valuable initiative."

The sites of new works are chosen solely from the point of view of facilities for transport and convenience in arrangements. Little attention is given to anything else. If workmen live a long way off they are brought to the works by boat or rail. If there are no towns about, one is built near the works for the

express purpose of attracting labor. . . . The number of workmen is very small compared with the dimensions of the works in which they are employed and the number of machines in use. Mechanical perfection is such that labor is reduced to a minimum, a large number of duties being limited to mere supervision. . . . Thus, in a refrigerating plant a single workman, seated in a hut, sets all the plant working.

There are technical libraries of great value in the works, containing periodicals, books, patent specifications, scientific papers and everything relating to industrial chemistry. Specialists are constantly engaged in reading and making notes under the instructions of the research experts.

Catalogues are printed in the works' own printing offices. These volumes are presented to all clients, and also to scientists and technical journals interested in the subjects. The extraordinary regularity in the development of each group of works is remarkable. At the famous "Badische" of "Bayer" the number of workmen has been about doubled every five years since the foundation. Immediately one particular line of manufacture is played out other productions are taken in hand. In new works there are, consequently, empty spaces near most of the machines, where others can be mounted when consumption attains a certain degree. Likewise, spaces are left between the buildings to erect other structures.

Purifying Water by Ozone.

The U. S. Consul General at Berlin, Germany, reports that ozone works for the sterilization of drinking water have been erected in the following European cities: Wiesbaden, Paderhorn, Hermannstadt and Chemnitz, in Germany; Paris, Nice, Chartres and Dinard, in France; Florence, in Italy, and St. Petersburg in Russia. He states that the plants in those cities are working satisfactorily. The process of ozonization effects a complete destruction of all bacteria of typhoid, cholera and dysentery that may be contained in the water. At the same time it is claimed that the number of so-called innocuous bacteria in the water is considerably diminished. The ozonization process may also be used on a small scale where sterilized or chemically pure water is desired. Portable apparatus is made in Berlin that can be used for the sterilization of drinking water intended for soldiers while in the field. Machines are also constructed for the ozonization of water in ice plants, in breweries, on board ship, or for any other purpose for which a limited amount of pure water may be demanded. A representative of a large concern manufacturing ozone apparatus claims that under ordinary conditions the approximate cost of sterilizing water on an extensive scale is about one-fourth cent per cubic yard. This estimate, however, refers only to the cost of operation after the plant has been installed. Experience up to the present time has demonstrated that the cost of ozone sterilization, inclusive of the preliminary filtration, is 1.6 to 1.8 pfennigs per cubic meter (about 1/2 ct. per cu. yd.), of

which amount the ozonization process itself costs the city approximately one-half.

Ventilation.

Three interesting papers on ventilation, one of the much neglected branches of chemical engineering, were presented before English societies last February. A paper on "Dust Explosives and Their Prevention" was presented before the Liverpool section of the Society of Chemical Industry by Dr. J. Harger; Dr. Leonard Hill and Dr. Martin Flach presented a paper before the Society of Art on "Ventilation," and Mr. Herbert A. Jones read a paper on "Automatic Temperature Regulation" before the Institute of Heating and Ventilating Engineers. The Chemical Trade Journal comments in the first two papers as follows: Dr. Harger's paper dealt with the subject of coal-dust explosions, and described a method of preventing these disasters, which had been worked out in the laboratories of the Liverpool university. These experiments have proved both that the only way absolutely to prevent dust explosions is to reduce the oxygen in the atmosphere to a few per cents below the normal, and that the ordinary atmosphere contains approximately 21.0 per cent of oxygen. It has been found that a reduction of 2 per cent would be quite sufficient for most mines. But to be quite safe, it was recommended that the amount of oxygen present should never exceed at any time $17\frac{1}{2}$ per cent. The value of Dr. Harger's suggestions, of course, depends entirely upon these results, and if it is quite correct that this slight reduction in the amount of oxygen has the effect of preventing explosions, then it is quite certain that a very decided step has been made in improving the safety of our coal mines. The point which will occur to most people is that this reduction in the amount of oxygen would have a very injurious effect upon the miners; but there is no doubt that our ideas upon the subject of what is necessary in this respect have long been in want of revision. According to Dr. Hill, a candle or an ordinary oil lamp will not burn in air in which the oxygen has been reduced to 17 per cent, but a man can perform continuous hard work in such an atmosphere and never notice any difference from ordinary air. It is not until the percentage is reduced to below 14 that any discomfort is realized. When the oxygen falls as low as 10 per cent then a dangerous point has been reached, and life cannot be maintained with the oxygen at $7\frac{1}{2}$ per cent. The influence of carbon dioxide on respiration is another matter in which many persons have been mistaken. It has been assumed, particularly by those pushing the sale of electrical heating apparatus, that any quantity of carbon dioxide in excess of a few parts per thousand acts as a poison; but it has been conclusively shown by such workers as Professor Haldane, Dr. Hill and other, that air containing any amount of carbon dioxide up to 1 per cent is just as good as ordinary air for breathing purposes. From the discussion which followed Dr. Harger's paper, it was evident that he had not convinced all his hearers of the practicability of his proposals, and for

our own part we should welcome a further set of experiments on a larger scale. From the importance of the question we have no doubt that this will soon be arranged. A method proposed by Dr. Harger for

How to Tell the Artificial Silks.

Artificial silk is fast coming to be a very important textile material and is being used in ever increasing quantities by the trade. It is employed as an adjunct not only to the silk industry itself but is also being used in connection with wool and cotton in the preparation of a great variety of fabrics. It is even being used largely in knot goods and hosiery in combination with cotton and mercerized cotton.

The dyer therefore is meeting more and more with this product, and as there are three different kinds of artificial silks in general use and as these different varieties possess certain differences in structure and quality it really becomes a question of considerable importance to the dyer to know one variety from another. This is more especially important because one silk may stand a treatment which would be fatal to another.

The three artificial silks now to be met with on the market are described in a recent issue of the *Wool and Cotton Reporter* as follows:

1. Collodion silk, known also as Chardonnet, or nitrosilk. It is prepared from nitrated cotton.
2. Cuprate silk, known also as Glanzstoff, Pauly, Elberfeld silk. It is prepared from a solution of cellulose in cuprammonium solution.
3. Viscose silk. This is prepared from a solution of cellulose in a mixture of caustic soda and carbon bisulphide.

In their outward appearance the three forms of artificial silk are so nearly alike that it would not be possible to distinguish between them. Even a microscopic examination by an experienced observer does not lead to any positive conclusion as to kind of silk.

A fairly simple test, however, according to *Paper* and one which may be easily carried out by the average dyer is the following: A sample of the silk to be tested is placed in a small porcelain dish and concentrated sulphuric acid is poured over the fibers. If the sample consists of collodion silk no coloration appears until about an hour has elapsed, when the acid solution will acquire a pale yellow color.

In the case of cuprate silk the acid becomes yellow immediately and the color becomes deeper on standing. In the case of viscose silk the acid immediately develops a reddish brown color, deepening to a rusty brown after standing for an hour.

BOOK REVIEWS.

Analysis of Metallurgical and Engineering Materials. By Henry Wysor, B. S. The Chemical Publishing Co., Easton, Pa.

This rather brief treatise is a very laudable striving to produce a work, the need of which is only too obvious. A strong and constantly revised book of this

sort is certainly demanded by the technical schools, the professional analysts and works laboratories.

Yet we dare consider Professor Wysor's effort as only breaking the way, a rather crude effort to attain what only a great master can successfully accomplish. We greet the compilation with the full credit due the pioneer.

A glance over the table of contents reveals the wide scope of the methods presented; we do not expect a man to write about an unfamiliar subject but as the work is intended to cover the *whole* field of "Metallurgical and Engineering Materials" one should needs study and make available the methods which may also be required in other than his own laboratory or by his own particular class of students.

We do not notice any references to the determination of gold, silver, and platinum; or to the analysis of the metals, such as lead, copper and spelter. Such omissions might be multiplied many times.

The presentation of the most suitable method may well call for considerable latitude in personal opinion and taste, yet, at the present time one would hardly expect to find presented such methods as the cyanide for copper or the copper potassium chloride method for carbon in iron.

The two written pages on the "Examination of the Microstructure of Iron and Steel" leaves us still wondering what we are looking at.

In his first calculation our author falls into an old error of significant figures. On page 10 he uses rounded atomic weights and then a quantity with 5 significant figures; by using only 3 figures in this quantity his result comes out 53.30% iron, the same as he would get 53.30% by using atomic weights, instead of his 53.35%.

The brief page on sampling ores by hand is not at all satisfactory. This is a topic so important and vital that a brief presentation is without value.

In general it is our opinion that any compendium of methods without critical notes and precautions loses its most important function. Especially for the student, a bit of history in the notes gives them new life.

At the present time there is considerable discussion about raising the standard of the chemical profession. This little book is a good illustration of the current practice to confine analysts to common laborers; that the book will be useful to such men goes without saying.—H. B. P.

Industrial Organic Chemistry. Fourth edition. By Samuel P. Sadtler. J. B. Lippincott & Co., Philadelphia. Price \$5.00.

Chemists who have been familiar with the earlier editions of Industrial Organic Chemistry by Dr. Sadtler will welcome the fourth edition of this work. The book has been thoroughly revised and represents the present status of chemical manufacture in the lines covered.

The descriptive matter in this book has always been of high class, and the chemist who is called upon to do analytical work on any of the products mentioned, will find that the analytical tests and methods described

here are quite satisfactory.

The book can be commended to students or practitioners of chemistry as one which is authentic and up to date.

Qualitative Analysis. By Baskerville and Curtman. The Macmillan Co., New York.

The general plan of this excellent text-book is as follows: (1) The general reactions of the common elements are studied. (2) Those reactions which are of the greatest analytical importance are studied from the point of view of the scheme of separation. (3) The scheme of analysis is given in detail, especial emphasis being given to the quantities of re-agents, their strengths and analytical manipulation in general. (4) The reasons for all operations, together with precautions and additional directions for the clearing up of doubtful results are given in the form of notes.

The scheme of analysis is well arranged, and the tests well adapted to the abilities of the immature student of chemistry.

At this time, when so many of the text-books of qualitative analysis are more like studies of the theory of electrolytic dissociation than of the analytical facts that the student must acquire for his further work in chemistry, it is a relief to find a good, thorough course in which the facts are set forth in their simplest form; the use or omission of that theory being left to the instructor's discretion.

The book is well printed on heavy dull paper and bound uniformly with the other chemical works published recently by the Macmillans.

Chemical Works; Their Design, Erection and Equipment. By S. S. Dyson and S. S. Clarkson. D. Van Nostrand Co., New York. Price \$7.50.

The preface of this work states that the authors have attempted to condense into a series of monographs the fruits of some twenty years' experience of the actual designing of chemical works and the selection of chemical plant. Their aim has been to present in each chapter a summary of sound practice and up-to-date construction.

If this has been their idea, they have fallen somewhat short of it in the work they have presented. The book is commended as possibly the best of its kind on the market, yet it leaves much to be desired. It contains the same stereotyped cuts supplied by manufacturers and the same set descriptions of the various machines and appliances which might be used in chemical works.

The descriptions of some of the plants are fairly good, such as the description of the Sulphuric Acid Plant. The Hydrochloric Acid Plant and the Nitric Acid plant.

There is, however, very little descriptive matter covering up-to-date appliances for general chemical processes, such as drying, evaporation, distillation, filtration, crushing and grinding. A number of cuts of such apparatus are given, yet so little descriptive matter is included, that the reader is left with no guidance to the selection of a satisfactory device.

Methods of Organic Analysis. By Henry C. Sherman. Second edition, rewritten and enlarged. The Macmillan Co., New York. Price \$2.40.

The purpose of this work is to give a connected introductory training in organic analysis, especially as applied to plant and animal substances and their manufactured products. The greater part of the book is devoted to quantitative methods for food materials and related substances.

The matter added to the second edition includes a chapter on solids and liquid fuels, sections on industrial alcohol, drying oils, crude petroleum, new international methods for glycerin analysis, and a quantitative method for the testing of Enzymes.

The book is valuable, as it has gathered together, under one cover, the most desirable methods which may be employed in the analysis and testing of the materials falling within its scope.

Not only methods of analysis are given, but also sufficient description is included to make clear the chemistry involved in the operations employed. Many references are also given to the original source of material.

The Metallography of Iron and Steel. By Albert Sauveur. Sauveur and Boylston, Cambridge; price \$6.00.

Professor Sauveur here presents us with a happy culmination of his long and distinguished services in acquainting us with metallography.

After the introduction and a most complete chapter on apparatus and equipment follow 24 lessons, each occupying from 8 to 29 pages, on the particular phases of the general subject. Appendix I is on manipulations and II on nomenclature.

A mere perusal of the headings of the individual lessons indicates the wealth of information displayed and the high attainments of the author as the subject has called him to delve in the more hidden depths of science and industry.

In offering such monumental work, every portion of which has demanded the utmost accuracy and painstaking study and personal research, the author certainly stands above criticism. From every point of view the work is complete and far in advance of the common conception of the subject.

The material of the book with the abundant reproduction, tables and diagrams is quite in keeping with text; to the intelligent it will be indispensable; to the student, instructor and practitioner, along many other lines, it will be invaluable. H. B. P.

A young Dutch chemical engineer with a diploma of the University of Delft wants a position as chemist. Address Box 43, % Chem. Engr., 608 S. Dearborn St.

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SOME INTERESTING OBSERVATIONS ON THE DISINFECTION OF LAKE WATER WITH CALCIUM HYPOCHLORITE.*

By DR. ARTHUR LEDERER† and FRANK BACHMANN.††

Ever since water was recognized as an important carrier of disease, the endeavor of sanitarians has been to make it safe for consumption. Guided by thorough bacterial research, and practical experiments by technical men, we are now in a much better position to appreciate the difficulties which have been overcome, and the questions still awaiting solution. As one would reasonably expect, the water problem has received the greatest attention. Until the last few years the study of sewage disposal was largely neglected, although the intimate relation of the problems has been recognized for a long time.

It is not surprising that Europe has been the leader in the protection of water supplies, but the congestion of the population abroad, and the long established centers of learning, accounts for this. Filtration of water supplies and emergency disinfection of sewages had been practiced there long before these protective measures were introduced in this country. How rapidly the filtration of water supplies in the U. S. has increased can be judged from figures stated by Geo. A. Johnson.¹ In 1890, less than 200,000 people were supplied with filtered water, in 1900, 1,860,000 and at present (1911), approximately 8,000,000. However, it is noteworthy that the protection thus afforded has not been altogether a voluntary prophylactic measure, but in most cases was forced upon the population by a heavy toll of death from typhoid fever. Approximately 35,000 people die annually in the U. S. from this disease.

It is said that the introduction of filtration has reduced the typhoid fever rate by about 75 per cent. The relation of an improved water supply to the mortality from other diseases in the U. S. can only be deduced imperfectly on account of the unsatisfactory methods of making death reports. In 1903 Hiram F.

Mills, of Lawrence, Mass., and A. A. Reincke, of Hamburg, noticed a distinct decline in the general death rate of those two cities, after the introduction of a pure water supply. Sedgwick and MacNutt² concluded from a thorough study of the death rate statistics of Lawrence, Lowell, Albany, Watertown, Binghamton and Hamburg, that death from gastrointestinal disorders and tuberculosis are distinctly reduced, while pneumonia, bronchitis and other infections are apparently diminished at the same time.

Allen Hazen stated in 1904, before the International Engineering Congress, at St. Louis, that the examination of the death rate of certain cities, which had improved their water supply, showed that for each death from typhoid fever prevented, two or three deaths from other causes are avoided. The reason for this phenomenon is not clear at present, and suggests a fruitful field for medical research. In a filter plant, ordinarily a bacterial reduction of 95 to 99 per cent may be obtained. Since the process is largely mechanical straining, the bacterial species are all reduced alike without selective action upon various species present originally, and the danger of infection is therefore reduced in proportion to the efficiency of the filter.

Sanitarians here and abroad have always looked favorably on the elimination of disease carriers by the direct addition of germicides to water supplies, particularly since the effluent of mechanical filters or slow sand filters, improperly operated, may contain many bacteria. Aside from sterilization by boiling, which is impractical on a large scale, various investigators have endeavored to sterilize water by the aid of halogens and their derivatives, by super-oxides, by copper compounds, permanganates, caustic lime, acids, etc. Lately the use of ozone and ultra violet rays has been undertaken with a degree of practical success as yet unascertained.

Of all the chemicals tried at present one alone serves best, that is chlorine, either as gas or in various combinations. Among the various disinfectants mentioned in the past, none is more efficient or economical of application than chlorine in the form most commonly used, viz., bleaching powder.

*Paper presented at the fourth meeting of the Illinois Water Supply Association, Urbana, Ill., March 5-6, 1912.

†Chemist and Bacteriologist, The Sanitary District of Chicago.

††Assistant Chemist, The Sanitary District of Chicago.

Hypochlorite Treatment of Public Water Supplies, Eng. Record, 1910, p. 821.

²On the Mills-Reincke Phenomenon and Hazen's Theorem Concerning the Decrease of Mortality from Diseases other than Typhoid Fever, Following the Purification of Polluted Water Supplies.—Jour. Infect. Diseases, Vol. VII., pp. 489-564.

The first Royal Sewage Commission used calcium hypochlorite for the deodorization of London sewage in 1854.⁸ As far back as 1885 the American Public Health Association endorsed it as the best disinfectant available, from the standpoint of cost and efficiency. In 1884 Dibdin again applied it to deodorize London sewage, but the results were unsatisfactory. Traube⁴ and Lode⁵ recommended Chlorinated lime, but Bassenge,⁶ Rabs,⁷ and Engels⁸ have not been favorable to its use in the quantities in which it has been applied. Hypochlorite was first used on a water supply on a large scale in Maidstone, Eng., in 1897, to clean the water mains following a typhoid fever epidemic, and again in 1904 and 1905 on the water supply of Lincoln, Eng. Chlorine preparations other than calcium hypochlorite were also tried at Guilford, Eng., at Middlekirk and Ostend in Belgium. Hünemann and Deiter⁹ recommend the use of sodium hypochlorite. The action of bleach upon specific bacteria has been studied by Nissen¹⁰ and a host of observers have directed their attention to its use in the disinfection of sewage. Among them were Proskauer, Elsner, Dunbar, Zirn, Schumacher, Schwartz, Kranepuhl, Kurpjuweit, Rideal, Dibdin, Fowler, Houston, Gage, Clark and Phelps. This list of observers is by no means complete including only a few of the investigators who have drawn favorable or unfavorable conclusions from the use of chlorine and its compounds for the sterilization of water or sewage.

A great impetus to the use of calcium hypochlorite for water in this country was given by the application to the water supply of Jersey City by C. A. Johnson, in June, 1908, and the use of hypochlorite in the Chicago union stockyards purification plant shortly afterwards. Since then the disinfection of water supplies by the aid of chlorinated lime, either alone or in connection with filtration, has progressed enormously. In every case where chlorinated lime has been intelligently applied the death rate from water borne diseases has decreased. Since some claim that the action of bleaching powder upon some pathogens is selective, a study of the influence on a disinfected water supply upon the mortality other than from typhoid fever would be instructive, just as has been done in the case of filtered water supplies. It seems fair to assume that the cases of tuberculosis would not be diminished, since that bacillus is very resistant to chlorine.

The reaction which takes place on placing chlorinated lime in water is fairly well understood. The hypochlorous acid is liberated by the free carbonic acid in the water. The hypochlorous acid in the presence of easily oxidizable matter breaks up into oxygen and hydrochloric acid, and the latter becomes immediately neutralized by the carbonates and bicarbonates.

The nascent oxygen which is liberated in the process is responsible for the destruction of bacteria and the oxidation of other organic matter which may be present. Since the available chlorine and the potential oxygen are in direct chemical relation, it suffices for practical purposes to designate the strength of a bleaching powder solution in p.p.m. of available chlorine, although it would probably be more correct to indicate its strength in p.p.m. of potential oxygen.¹¹

There is still some question as to the so-called "residual chlorine" left in water after disinfection. It is supposed that the residual chlorine is not chlorine in its free state, but a loose combination of hypochlorous acid and organic matter. The oxidation of mineral salts by bleaching powder is, as a rule, not a matter of great importance in the disinfection of water supplies. In a highly polluted water or a sewage, however, much of the available chlorine may go to oxidize mineral constituents or gases in solution before the bacteria are attacked. The effluent of a biolytic tank at our sewage testing station absorbs as high as 20 p.p.m. of available chlorine without showing a material reduction in the number of bacteria. The chlorine merely oxidizes its equivalent of hydrogen sulphide in the sewage.

The free carbon dioxide in the water is always reduced after disinfection with hypochlorite. The total solids and the hardness are slightly increased. Coloring matter, if present, is not noticeably reduced, neither is turbidity affected. The organic matter is lessened when judged by the oxygen consumed test. Even the best grades of bleaching powder contain impurities, such as calcium chlorate, calcium hydrate, calcium carbonate, calcium sulphate, etc.

In late years the shores of the Great Lakes have become polluted by sewage so that Erie, Toronto, Cleveland, Milwaukee and other cities have resorted to emergency disinfection. The quantity of "hypo" required by a water will largely depend upon its quality and the degree of contamination. Variations in turbidity will also affect it, particularly when the suspended matter is rich in organic matter. Bartow and Birdsall¹² refer to a case at Fort Sheridan, Ill., where a high turbidity in the water was observed to be accompanied by an increase in diarrheal diseases. The turbidity is greatest during stormy seasons. Observations made by Pearse, Tonney and Bartow,¹³ in a survey of Lake Michigan extending from Chicago to Waukegan, showed that in-shore the turbidity may reach 180 p.p.m. One and two miles off-shore, however, the turbidities were low, ranging from zero to 29 for average figures. Beyond a depth of 60 ft. the turbidity was always under 5 p.p.m. This depth occurred from 3 to 5 miles off-shore. "Practically all the intakes from Gary, at the small end of Lake Michigan to Waukegan, are in a zone of turbid water." Bartow and Birdsall¹² found the ranges of turbidity at

⁸Second Royal Sewage Commission, London, 1861.

⁴Zeitsch. f. Hyg., 1894, p. 149.

⁵Arch. f. Hyg., 1895, p. 236.

⁶Zeitsch. f. Hyg., 1895, p. 227.

⁷Hyg. Rundschau, 1901, p. 1085.

⁸Zentr. bl. f. Bakt., 1902, p. 495.

⁹Deutsch. med. Wochenschr., 1901, p. 391.

¹⁰Zeitsch. f. Hyg., 1890, p. 62.

¹¹Charles G. Hyde, "The Sterilization of Water Supplies by the use of Hypochlorites," a paper presented to the Santa Barbara meeting, League of California Municipalities, Oct. 28, 1911, p. 10.

Lake Forest between 2 to 170 p.p.m., and at Evanston between 5 and 200 p.p.m. C. A. Jennings¹⁴ reports a low average turbidity at Erie, Pa., as well as a low content of bacteria and organic matter. The water supply in Charlotte N. Y.,¹⁵ taken from Lake Ontario is reported as having an average turbidity of 11.3 p.p.m. Aside from variations in turbidity the chemical composition of the unpolluted waters of the Great Lakes is fairly constant, with the exception of Lake Superior, as shown by the analyses of R. B. Dole and R. G. Roberts.¹⁶

The quantity of "hypo" applied on a quiet day may not suffice in a storm when the turbidity is high, unless settling basins are provided, as at Erie, Pa. When the turbidity is high it is easily conceivable that "hypo" treatment with the same amount as in low turbidity would only be partly if at all effective. Turbidity usually carries with it an abnormally large quantity of easily oxidizable organic matter, and the coarser suspended particles may harbor millions of bacteria which, thus protected, would escape destruction. In other words, disinfection by itself can not take the place of filtration. It might if the water supply is always clear, and of uniform quality. In the use of ozone and the ultra violet rays turbidity decreases the efficiency of the method.

Depending upon local conditions, the quantity of bleach applied at the different cities bordering on the Great Lakes varies between 0.2 to 0.4 p.p.m. available chlorine, with the exception of Cleveland, which is using a larger quantity at present. Tests made at our laboratory demonstrated that for slightly polluted water from a 3-mile crib, 0.3 p.p.m. of available chlorine is an ample quantity, and that the time of contact need be very short. Under laboratory conditions, the action is almost instantaneous, but for practical purposes, sanitary engineers recommend a contact period from one-half to one hour. 0.3 p.p.m. and often 0.2 p.p.m. is sufficient to eliminate all gas-formers, when the water is fairly clear. The reduction of the total number of bacteria is around 97 per cent. The frequent occurrence of spreaders on litmus lactose agar plates is in line with observations made in many places. The "resistant minority" to which spore bearing spreaders, like *B. subtilis*, belong, does not permit a bacterial reduction of 100 per cent with the quantities in which bleach is ordinarily applied.

Since the use of disinfection at the stock yards filter plant in Chicago work, largely of a bacterial nature, has been done in this country on the question of disinfection of contaminated supplies and sewages, in particular by Phelps.¹⁷ Where a comparatively small

quantity of sewage is polluting a large water supply, or where sewage is likely to contaminate shell-fish beds, disinfection of sewage may serve a useful purpose. Proof is ample that the typhoid fever bacillus will thus be eliminated, but two serious objections to the method arise: First, the large quantity of organic matter in the disinfected sewage may at any time serve as a culture medium to pathogens under favorable conditions, and second, the pathogenicity of some of the sewage bacteria is either unknown or little understood. Moreover, the germicidal effect of "hypo" upon sewage bacteria has not been sufficiently investigated. In speaking of sewage bacteria, we should remember that although some types have been found in waters and nowhere else, there is really no limit to the variety of species which a contaminated water may contain. Some of the known pathogenic bacteria have as yet not been isolated in a polluted water supply, largely on account of the immense dilution and imperfect working methods. In fact sewage may contain all bacteria known to men, pathogens as well as saprophytes. Consequently the action of bleach upon all of these micro-organisms should interest the sanitarian. The saprophytes must not be overlooked because their relation to disease is by no means settled.

The bacterial flora of Lake Michigan tap water of Chicago was investigated twelve years ago by Zeit and Fütterer¹⁸ jointly, when the city of St. Louis tried to enjoin Chicago from emptying its sewage into the Illinois river. They found in 7 samples the *B. coli* communis on three occasions, the *B. lactis aerogenes* once. Their conclusion was that *B. coli* communis may be found in water without sewage pollution, and that it may or may not be virulent. Thirteen non-pathogenic species were isolated, among them *B. subtilis* 4 times, and *B. mesentericus* 3 times.

The presence of *B. coli* in a water supply is generally accepted as indicative of fecal pollution, and many studies have been made to compare the viability of this bacillus to its dreaded companion, the typhoid fever bacillus. The evidence shows that both species are of a low resistance, and the elimination of one coincides with the elimination of the other.

In the disinfection of a water with "hypo" the claim is made that the action upon types of intestinal bacteria as *B. coli* and *B. typhosi* is a selective one. Phelps¹⁷ made emulsions of the two species in tap water, and applied on the average 5 p.p.m. of available chlorine. In a general way the result of his experiments indicate that "*B. coli* may reasonably be regarded as test organisms in disinfection work, and that the process may be expected to destroy typhoid organisms present, at least as thoroughly." Working on the disinfection of trickling filter effluents at Baltimore, Md., with chlorinated lime, Phelps observed that the removal of *B. coli*, as indicated by the ferment-

¹²Composition and Treatment of Lake Michigan Water.—Second Report of the Lake Michigan Water Commission, p. 69.

¹³Report on Sanitary Survey of Lake Michigan, Chicago to Waukegan.—Second Report of the Lake Michigan Water Commission, p. 37.

¹⁴Typhoid Fever Epidemic at Erie, and Hypochlorite of Lime Treatment Plant at Erie.—Engr. Record, 1911.

¹⁵The Rochester & Lake Ontario Water Company's Filters.—Engr. Record, 63, p. 626.

¹⁶The Waters of the Great Lakes. Paper presented before the Am. Pub. Health Assn., at Winnipeg, Man., Aug., 1908.

¹⁷The Disinfection of Sewage and Sewage Filter Effluents. U. S. Geol. Survey, Water Supply and Irrigation Paper, 229.

¹⁸Ill. State Board of Health, "Report of the Sanitary Investigations on the Ill. River and its Tributaries, 1900, p. 85.

tation test, did not coincide with the removal of acid forming bacteria on the plate. The removal of the *B. coli* on the plate seemed to be better than indicated by the fermentations. Efforts to discover the discrepancy were but partly successful. Identification of *B. coli* seemed to indicate that many of the positive tests for fermentation were due to the presence of a fermenting organism other than *B. coli*.

In this connection some of our observations may be of interest. In applying the solution of chlorinated lime to an emulsion of *B. coli* in Lake water, we noted repeatedly that a number of the colonies of *B. coli* on the plates after disinfection did not present the original appearance, but were much smaller than at the start, and failed to produce acid. We are unable to account for the failure of the colonies to turn red on litmus lactose agar. The amount of chlorine is much too small to exert a bleaching effect, and the alkalinity is too slight to neutralize the organic acids formed. The probable explanation is the diminished virility of the bacilli. They may be temporarily "stunned," and it is likely that they become rejuvenated under favorable conditions. The colon bacillus in the water, by itself, is not considered detrimental. Some investigators maintain that the colon bacillus is somewhat of an intestinal scavenger. Where numerous colonies of pathogenic organisms can be cultivated from feces we may find a diminished number of colon bacilli. This condition may be observed in infections with the organisms of dysentery, cholera, typhoid and paratyphoid. Some consider that the *B. coli* produce a bactericidal substance which inhibits the growth of or destroys pathogenic bacteria which may have passed the gastric juices.¹⁹

Of the many varieties belonging to the colon group, more must be learned before we can speak with authority on that subject. We do not regard our study of the effect of "hypo" upon colon bacilli as concluded, but wish to record our observations. More detailed work can be taken up at a future date. It has been noted by J. W. Ellms²⁰ in the disinfection of Ohio river water that certain saprophytes multiplied profusely after disinfection with chlorinated lime, and one of Ellms' conclusions is that bleaching powder is apparently not a true sterilizing agent, but rather one which inhibits bacterial growth upon culture media. It would seem that this would apply also to bacteria other than of the spore bearing type.

On using a lake water emulsion containing a pure culture of *B. coli* the reduction with 0.3 p.p.m. available chlorine amounted, as a rule, to 99.6 per cent after the first 5 minutes. The initial counts varied in the different experiments from 3,000 to 500,000 in 1 c.c. A blank was always made on the lake water without a bacterial emulsion.

We would like to emphasize that percentage reduction figures are not of such great importance as the

initial number of the bacteria. With one and the same water supply such figures may serve as an index of the efficiency of a "hypo" plant. Where different sources of water supply are treated the difference in the bacterial flora might account for differences in percentage reduction figures. Furthermore, in an artificial bacterial emulsion the percentage reduction will appear greater the larger the initial count has been. It is not likely, however, that the difference would be material, since our experiments and the experiments of others have shown that with a sufficient quantity of chlorine the reduction of *B. coli* has been fairly uniform whether the initial count was high or low. For practical purposes it seems that it is not so important to try to obtain a reduction of 99 per cent, instead of 97 per cent, or thereabouts, as it is to obtain information on the pathogenicity of the residual number. There is also danger of introducing small quantities of organic matter or other oxidizable matter with the emulsion. Possible this would coincide with the small amount of organic matter present in a contaminated sample.

Similar experiments with a number of pure cultures of bacteria likely to be present in contaminated water and sewages are of interest.

A number of spore bearing bacteria were treated in a like manner, and varying quantities of "hypo" were applied in order to test their viability under such conditions. N. S. Hill, Jr.,²¹ states that bleaching powder applied as a disinfectant to water does not destroy spore bearing bacteria, such as *B. aerogenes capsulatus*, *B. butyricus* and *B. cadaveris sporogenes*. The culture taken for our experiments were *B. subtilis*, *B. mesentericus rosei*, *B. mesentericus fuscus*, and *B. anthracis*. Only the last one is considered pathogenic to man. The difficulty of eliminating the spores of *subtilis* has always been a source of annoyance. As high as 400 p.p.m. of available chlorine did not entirely eliminate the colonies. The following table shows the percentage reduction obtained with various amounts of "hypo."

TABLE I.—PERCENTAGE REDUCTION OF *B. SUBTILIS* ON DISINFECTION WITH CALCIUM HYPOCHLORITE.

15 min. Contact Initial Count 450 in 1 c.c.	
p. p. m. Avail. Chlorine.	Percentage reduction.
25	3
50	43
75	50
100	75
200	89
300	93
400	95

The large amounts of chlorine necessary to obtain a material reduction in the number of the so common *B. subtilis* illustrates better than anything else the impossibility of obtaining sterile plates with the amounts ordinarily applied. The spores of anthrax which belong to the same group seem to be very much less resistant to chlorine. 50 p.p.m. of available chlorine

¹⁹E. R. Stitt, "Practical Bacteriology, Blood Work and Animal Parasitology," p. 91.

²⁰Effect of Bleaching Powder upon Bacterial Life in Water." Eng. Record, 63, 471.

²¹Bleaching Powder as an Agent in the Purification of Water. Eng. Record, 63, 491.

nearly eliminated it, while 100 p.p.m. resulted in a sterile plate. The period of contact was 15 minutes, just as in the case of all other species, this being considered ample from a working standpoint. The experiments with *B.anthraxis* are of more theoretical than practical interest. Infection of man from a water supply containing anthrax is very remote. The bacillus has been isolated, however, in a contaminated water on numerous occasions. Zeit and Fütterer¹³ found anthrax twice in the Illinois river at Havana. Statements of the quantities of chlorine necessary to destroy the bacillus differ greatly in various text books and journals.

TABLE II.—PERCENTAGE REDUCTION OF ANTHRAX SPORES ON DISINFECTION WITH CALCIUM HYPOCHLORITE.

15 min. Contact Initial Count 12,000 in 1 c.c.

p. p. m. Avail. Chlorine.	Percentage reduction
10	95.8
15	97.7
20	99.3
30	99.5
50	99.9
100	100

Much smaller quantities of "hypo" were necessary for the destruction of other spore bearing bacteria.

TABLE III.—PERCENTAGE REDUCTION ON DISINFECTION OF SPORE BEARING BACTERIA WITH CALCIUM HYPOCHLORITE.

p. p. m. Avail. Chlorine.	15 Min. Contact	
	200 in 1 c.c. <i>B. Mesenter rosei.</i>	1900 in 1 c.c. <i>B. Mesenter fuscus.</i>
0.1		
0.3		
0.5		
0.7		
1.0		
2.0		
3.0		
4.0		
5.0	80.0	26.4
10.0	75.0	31.6
15.0	80.0	52.7
20.0	100	60.6
30.0		60.6

There seems to be a great difference in the resistance of various spore bearing species towards chlorinated lime. Checks on the results have not always given the same percentage reduction, but the figures coincide closely enough to the results tabulated.

Not only the aerobic spores but also the anaerobic spores are very resistant to chlorine. On disinfecting a sample of sewage with as much as 10 p.p.m. of available chlorine, spores developed on incubation in the Novy jar. The well known anaerobic spore bearer—the tetanus bacillus—has been isolated by Zeit and Fütterer in the Illinois river at Morris and Henry, Ill., and in the Spoon river at Havana, Ill.

The important group of intestinal bacteria is much less resistant than the spore group, as might be expected. The *B.mirabilis*, belonging to the proteus group has proven an exception, suggesting the presence of spores. Even 5 p.p.m. of available chlorine has not entirely eliminated the bacillus. The other figures indicate, however, that even under severe conditions 0.2 p.p.m. of available chlorine is sufficient for practical purposes. The effect of chlorine upon

the *B.typhosus* has been exhaustively studied by various investigators, and it has therefore been omitted from our work.

TABLE IV.—PERCENTAGE REDUCTION ON DISINFECTION OF THE GROUP OF INTESTINAL BACTERIA WITH CALCIUM HYPOCHLORITE.

p.p.m. Avail- Chlor- ine.	15 Min. Contact.					
	160,000 in 1 c.c.	9,500 in 1 c.c.	3,000 in 1 c.c.	8,000 in 1 c.c.	180,000 in 1 c.c.	500 in 1 c.c.
B. faec. cloacea.		99.98				
B. type. mirabilis.		99.99	99.97	27.3	99.83	99.17
Prot. enter- itidis.		100	100	63.7	99.98	99.98
B. lactis aerog.				72.7	100	100
B. choler- suis				63.7		
0.1				63.7		
0.2				63.7		
0.3				90.9		
0.5				90.9		

Two chromogenic species, the *B.pyocyaneus* (green pus bacillus), and *sarc.lutea* were tested for their resistance. 0.3 p.p.m. of available chlorine proved sufficient to eliminate both species. *B.acidi lactici* was likewise completely destroyed by 0.3 p.p.m. of available chlorine.

Time did not permit us to follow the investigation further. In a general way the results coincide with the work of other observers, and with the assumption that all but the hardier species, such as the spore bearers, are effectively destroyed with quantities of hypo as ordinarily applied.

A question which may possibly be asked in connection with the disinfection of lake water is in regard to the rate of bacterial destruction under winter and summer conditions. The lake water temperature at Chicago may vary 36° F. from summer to winter. Disinfection with chlorinated lime is a chemical process, and as such is facilitated by higher temperature. Other conditions being equal, we have to consider that during winter conditions the bacterial content in the lake is lower and the dissolved oxygen higher. This would seem to indicate that less chlorine would be needed in winter. Phelps¹⁷ in his work on the disinfection of sewage and filter effluents, considered the amount of oxygen present as an important index to the character of the sewage or the effluent in reference to its effect on chlorine. He found the disinfection of the oxygenated filter effluent much less influenced by temperature changes than de-aerated sewage. In the light of his observations it seems fair to assume that with the highly stable lake water, even if contaminated, temperature changes would make but little difference. We have made some experiments on this question and found the assumption to be correct, when the customary quantities of "hypo" were applied. Sterile flasks containing 100 c.c. of Lake Michigan water were artificially contaminated, each with the same number of *B.coli* in one case, and *B.acidi lactici* in the other. They were brought to a temperature of 32, 50 and 69° F., and then treated with 0.2 and 0.3 p.p.m. of available chlorine. Samples were plated out on litmus lactose agar after 5 minutes, 15 minutes, 30

minutes and one hour. The various counts showed slight differences, but no systematic increase or decrease in the number of bacteria could be recorded in any case. The lake temperature, as a rule, does not go above 68° F. in summer and therefore there seemed no need for carrying on the experiments at a higher temperature. Still there is a possibility that a higher temperature would tend to bring out differences in the rate of bacterial destruction. J. W. Ellms²⁰ demonstrated, on disinfecting Ohio river water, with a hypo solution containing 0.2 p.p.m. of available chlorine, that a lower temperature retarded the rate of disinfection. His observations refer to temperatures ranging from 38 to 89° F.

The most important question confronting the sanitarian is a possibility of a taste in the disinfected water. Nothing has discredited the "hypo" treatment more than excessive doses, accidental or otherwise. In many cases the quantity of "hypo" may have been reduced to an unsafe minimum either on account of such mishaps in the application, or on account of popular prejudice. The idea of drinking disinfected water seems to be repugnant to the broad masses. Of late, however, thanks to the educational campaign carried on by people interested in public health, and by progressive journals, the prejudice against the use of "hypo" is decreasing. When properly applied, the taste of sterilized water is mainly the result of auto-suggestion. This can readily be proven in a practical test, as carried on in our laboratory. At one time, we took a squad of 8 men, none of whom had ever tasted "hypo" in water before, prepared a series of bottles containing lake water with various quantities of "hypo" and distributed a number of blank bottles containing lake water among the "hypo" samples. When a water supply is treated with "hypo" the consumer expects to taste "something" in the water. That is the frame of mind also in a laboratory test. As might be expected, a number of the squad tasted "something" in lake water containing no "hypo" at all, and one man even discovered an odor in one of the blanks. Recently we repeated the test in order to check the results first obtained, in regard to the limit of noticeable taste and odor. The results coincided fairly well with the earlier ones.

We have been impressed with the necessity of certain precautions, in order to make such a physiological test a success. A chemical laboratory is a poor place for such a test. The laboratory worker being constantly in an atmosphere more or less saturated with odors foreign to pure air, grows accustomed to such conditions, and is likely to miss an odor or taste, no matter how slight, which would be suggested to a man unaccustomed to laboratory conditions. Care must also be taken to rinse the mouth thoroughly with pure water after tasting each sample. If one were to start with the lowest concentration and consecutively taste the samples, gradually increasing the strength, he would probably pass a sample which he might

have detected had he rinsed his mouth with pure water each time. It is much better to start, say with 0.1 p.p.m. and then pass right on to the 0.4 p.p.m. sample. If there is a slight taste he is likely to detect it much better than if he would have sampled the 0.2 and 0.3 water. A squad representative of the average grade of people must also be selected. The chlor-

TABLE V.—OBSERVATIONS AS TO TASTE AND ODOR OF LAKE MICHIGAN WATER CONTAINING VARIOUS AMOUNTS OF FREE CHLORINE. FEB. 27, 1912.

Serial No. of Sample.	p.p.m. Available Chlorine.	Observer.						
		1	2	3	4	5	6	
I.	0.0	—	—	—	—	—	—	Taste
		—	—	—	—	—	—	Odor
II.	0.1	—	—	—	—	—	—	Taste
		—	—	—	—	—	—	Odor
III.	0.2	—	—	—	—	—	—	Taste
		—	—	—	—	—	—	Odor
IV.	0.3	—	—	—	—	—	—	Taste
		—	—	—	—	—	—	Odor
V.	0.4	?	—	—	—	—	?	Taste
		—	—	—	—	—	—	Odor
VI.	3.0	+	—	+	?	—	+	Taste
		—	—	—	—	—	—	Odor
VII.	0.6	+	—	+	?	—	+	Taste
		—	—	—	—	—	—	Odor
VIII.	0.7	+	+	+	+	—	+	Taste
		—	—	—	—	—	—	Odor
IX.	0.8	+	+	+	+	—	+	Taste
		—	—	—	—	—	—	Odor
X.	0.9	+	+	+	+	?	+	Taste
		+	—	—	—	+	+	Odor
XI.	1.0	+	+	+	+	+	+	Taste
		+	+	+	+	+	+	Odor
XII.	2.0	+	+	+	+	+	+	Taste
		+	+	+	+	+	+	Odor
XIII.	3.0	+	+	+	+	+	+	Taste
		+	+	+	+	+	+	Odor

ine is tasted long before its odor is noticed. Since the claim is often set forth that in the application of hypochlorite, other substances in addition to the chlorine may be responsible for the acrid taste, a

TABLE VI.—OBSERVATIONS AS TO TASTE AND ODOR OF LAKE MICHIGAN SLICKY SLOIHY ONINIVLNOJ RELVAM NVQ CHLORINATED LIME. FEB. 27, 1912.

Serial No. of Sample.	p.p.m. Available Chlorine.	Observer.						
		1	2	3	4	5	6	
I.	0.0	—	—	—	—	—	—	Taste
		—	—	—	—	—	—	Odor
II.	0.1	—	—	—	—	—	—	Taste
		—	—	—	—	—	—	Odor
III.	0.2	—	—	—	—	—	—	Taste
		—	—	—	—	—	—	Odor
IV.	0.3	—	—	—	—	—	—	Taste
		—	—	—	—	—	—	Odor
V.	0.4	+	?	—	—	—	—	Taste
		—	—	—	—	—	—	Odor
VI.	0.5	+	+	—	+	—	—	Taste
		—	—	—	—	—	—	Odor
VII.	0.6	+	+	—	—	—	—	Taste
		—	—	—	—	—	—	Odor
VIII.	0.7	+	+	?	—	—	—	Taste
		—	—	—	—	—	—	Odor
IX.	0.8	+	+	+	—	—	—	Taste
		—	—	—	—	—	—	Odor
X.	0.9	+	+	+	—	?	—	Taste
		—	—	—	—	—	—	Odor
XI.	1.0	+	+	+	+	+	+	Taste
		—	+	—	+	—	—	Odor
XII.	2.0	+	+	+	+	+	+	Taste
		?	+	+	+	—	+	Odor
XIII.	3.0	+	+	+	+	+	+	Taste
		+	+	+	+	+	+	Odor

series of samples was arranged containing various quantities of free chlorine gas in solution, the gas being prepared by the action of sulphuric acid upon bleaching powder.

The accompanying tables (V and VI) show the difference between the taste and odor observed by our squad, when using chlorinated lime and also free chlorine.

If we make allowance for individual mistakes, we are justified in stating that there is no material difference between the taste of free chlorine and "hypo." The average is somewhere around 0.6 p.p.m. of available chlorine, but 0.5 p.p.m. can often be detected. It seemed, however, that the odor of the gaseous chlorine sample was detected sooner than it was in the "hypo" sample. To identify the odor, on the average, 1.8 p.p.m. of available chlorine was required in the bleaching powder sample, and 0.9 p.p.m. in the free chlorine sample. The free chlorine is perhaps more volatile in a water thus treated, and the water would rid itself quicker of the odor of the chlorine than in the "hypo" treated sample. The tasting squad consisted of six people. They were set to work a few minutes after the preparation of the various dilutions. The time element is to be considered. The water treated with "hypo" or chlorine will lose its taste and odor in due time, depending upon the concentration. Our results are in harmony with some experiments carried on at the laboratory of the Illinois State Water Survey. Van Brunt²² claims that about 0.6 p.p.m. of available chlorine could be tasted.

In closing we wish to state our opinion that the process of hypo disinfection has great merit from a practical working standpoint as well as from the standpoint of the sanitarian. It is cheap, but it can not supplant filtration except under favorable circumstances. It seems effective as a germicide, but the relation of "hypo" sterilization to mortality statistics other than typhoid fever still remains to be demonstrated.

In a paper presented at the recent International Congress of Applied Chemistry Mr. J. W. Turrentine, of the Bureau of Soils, reported a great number of potash determinations on brines from various sources and then stated that his conclusions were as follows: From theoretical considerations it appears improbable that the known deposits of rock salt in the United States east of the Rocky Mountains are associated with potassium salts other than small amounts occluded and absorbed during crystallization of the sodium chloride. In no cases do the artificial or natural brines or their concentrates contain sufficient potash to make them of commercial value. Certain Western desert-basin brines suggest interesting possibilities of these. Searles Lakes, San Bernardino County, Calif., and Railroad Valley, Nevada, are the best, showing over 6 per cent of K_2O content in the total salts. The sea-water bitterns, when evaporated, give commercially valuable manure salts, but the amounts of the mother liquors are too small to make a production comparable with the country's total consumption.

THE LATEST ACHIEVEMENTS AND PROBLEMS OF THE CHEMICAL INDUSTRY.*

By CARL DUISBERG.

Probably in no domain of human knowledge and endeavor have the combined forces of theory and practice, intimately acting and reacting upon each other, made such immense strides and led to the solution of such difficult problems as in the chemical industry, an industry which, indeed, had its beginnings in the distant past, but in its vast development and international character is essentially a child of modern times. Success has so emboldened this industry that it considers itself capable of solving any problem, provided the men in its service are well trained in theory and practice and ready to devote themselves to the best of their ability, with patience and perseverance, to the object in view. This has been shown by the struggle between the contact process of producing sulfuric acid and the old "chamber process," by the rivalry between the Solvay process and the Le Blanc method in the manufacture of soda; by the production of nitric acid and its salts by direct oxidation of nitrogen of the air under the influence of the heat of the electric discharge; by the manufacture of ammonia from atmospheric nitrogen indirectly *via* calcium cyanamide, and directly by combination with hydrogen; by the replacement of madder by alizarine, and of natural by synthetic indigo, as well as by innumerable other instances in the color, perfume and pharmaceutical industries.

If I venture before an audience not wholly consisting of chemists, within the brief period of an hour, to describe the latest achievements of the chemical industry and to recount the problems that are engaging our attention, I must restrict myself to a great extent both in the choice of the subject-matter and its mode of presentation. We can, indeed, merely touch upon the most important happenings in our industry and must, from the very outset, refrain from a thorough discussion of the subject, either from the purely chemical or the technical side. However, what cannot be described for lack of time, and what we should very much like to add for the sake of those chemists who are present, is illustrated by our rich collection of diagrams, products and materials of all kinds. What can neither be mentioned in my paper nor illustrated by these exhibits, will be demonstrated by means of lantern slides, and, should you possess patience enough, I shall show you at the conclusion of my address one of the newest factories which the German Chemical Industry has built on the Rhine, with its various manufacturing departments, and, above all, its provisions for the welfare of its employees.

In the spirit of Faust, "Who brings much will bring something to many," I invite you to make a flight with me in an airship, as it were, over the fields where the

*General lecture by Geheimerr Regierungsrat Prof. Carl Duisberg, managing director of the Farbenfabriken of Elberfeld Co., delivered at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

²²Univ. of Ill. State Water Survey Bulletin 8, 53.

Chemical Industry holds sway and, from our point of vantage, to take a bird's-eye view of the latest achievements of this industry. Now and then we shall make a landing and examine the most attractive features a little more closely.

Production of Power.—The question of power, which is of the utmost importance in every industry and especially in the great synthetic processes by means of which nitric acid and ammonia are manufactured, is now dominated by the perfected utilization of hydraulic power and the development of the turbine. Not only does the transmission of electric energy render it possible to utilize water power at great distances, but it also permits the transmission of power evolved at the coal mines and the peat fields to distant points, thus eliminating the necessity of transporting the fuel itself. Recently we also learned to apply the principles of the water turbine to the steam turbine. But this advance over the piston steam engine, which Watt so ingeniously constructed about 150 years ago, has already been surpassed by benzine, petroleum or oil motors (Diesel motors), and above all, by the reliable gas engines, which are driven by blast furnace gases, Mond gas, and, more recently, by peat gas.

Production of By-Products.—The manufacture of by-products goes hand in hand with this more direct generation of energy from fuel. These products include ammonium sulphate, of such great importance in agriculture, and the tar distillation products so indispensable in the color industry. The latest and most rational method of utilizing the peat or turf beds, so plentiful in Germany and in many other countries, is practiced in Schweger Moor near Osnabruck according to a process discovered by Frank and Caro. There, peat gas is produced and utilized and ammonia obtained as a by-product, the required power being generated in a 3,000-h.p. central electric power station. The moorland, after removal of the peat, is rendered serviceable for agricultural purposes.

At that place, nearly 2,500-2,600 cubic meters of gas with 1,000-1,300 calories of heat were obtained from 1,000 kg. of absolutely water-free peat in the form of air-dried peat with 45 to 60 or 70 per cent. of moisture. This gas represents energy equal to 1,000 h.p. hours, equal to 700 kilowatt hours, after deducting the heat and power used for the operation of the gas works. In addition 35 kg. of ammonium sulphate were produced from the above quantity of peat which contains 1 per cent. of nitrogen.

The greatest problem of power production, the direct conversion of coal into electric energy by means of gas batteries, a problem which we had hoped to solve 25 years ago, is still today nothing more than a dream.

Production of Cold.—Besides the problem of power and heat, the question of refrigeration is one of growing importance to the chemical industry. Instead of the ammonia machines with which a temperature of -20° C. can be attained, we employ today sulphurous acid machines, or, better still, resort to the carbonic

acid gasifier, which yields a temperature of -40° C. It is hoped in the near future to produce refrigerating machines, which, by the use of suitable hydrocarbons, will give temperatures of -80° C. Plants for the liquefaction of air, producing as low a temperature as -190° C., are becoming more and more common and are especially profitable where gas mixtures, rich in oxygen, or where pure nitrogen, which is simultaneously produced, can be utilized. Diagrams showing the process invented by Linde for the rectification of liquid air with the object of isolating nitrogen and oxygen are exhibited here. The Badische Anilin and Soda Fabrik in Ludwigshafen on the Rhine intends to manufacture hydrogen from water gas in a similar way and to utilize the carbon monoxide, which is simultaneously obtained, as a source of power. In a large plant which is being erected, the firm is going to produce ammonia synthetically by combining, according to Haber's invention, pure nitrogen, obtained by the liquefaction and rectification of air, with hydrogen manufactured as above. Particulars about this process will be given during the Congress by Professor Bernthsen in his lecture on "Synthetic Ammonia."¹

Size of Apparatus.—Influenced by the Solvay process for the manufacture of soda and its pecuniary advantages, the apparatus used in the chemical industry has enormously increased in size. In this respect the United States, no doubt on account of the example set by the iron industry with its blast furnaces with a daily capacity of 500 tons, its giant conveyers, its huge hoisting cranes, is ahead of other countries. But careful calculations have proved that there is a limit in this direction. The failure, on account of size, of the Mac-tear sulfate furnace, with a daily output of 25 tons, is well known, while the mechanical sulfate furnace of the Verein Chemischer Fabriken in Mannheim, which produces only 7 tons a day, is a success everywhere. It is not improbable that the high cost of construction and the great loss which accidental stoppage entails will necessitate a reduction in size of the wonderful Wedge furnace, a creation of the United States, which roasts 30 tons of iron pyrites per day.

In the organic chemical industry, the iron vessels for chlorination, sulfonation, nitration, reduction and oxidation, as well as the wooden tanks in which we diazotize and produce colors, have developed from the small vessels and vats of former years into apparatus of mighty size, their limit being generally determined by the capacity of the mechanical industry. But here, too, the mistakes which often occur in manufacturing processes and the extra losses which they involve, teach us that a wise moderation should be exercised.

Wherever possible, continuous operations have replaced those processes which worked intermittently. In this way loss of time and expense, caused by cooling and reheating, are avoided. This is exemplified by Uebel's new method of the production of nitric acid from Chili saltpetre with retorts lying above each

¹The Chemical Engineer, November, 1912.

other and without stirrer, and by that of the Badische Anilin and Soda Fabrik, where the chambers are back of each other with stirrer, these methods having replaced the old single retort process.

Materials for Apparatus.—As regards materials for chemical apparatus several new wares must be referred to:

Apart from the fact that the saltpetre industry of Norway taught us how to absorb dilute nitrous gases in towers 20 meters high, made of granite, a substance which was rarely used for chemical purposes, we have today at our disposal tubes, dishes and vessels of fused quartz, which are stable against acids and heat and which are manufactured in the same sizes and dimensions as the well-known earthenware vessels.

The greatest progress, however, has been made in the manufacture of iron alloys or refined steel. Thanks to the kindness of Friedrich Krupp, of Essen, I am in the fortunate position to describe a large number of hitherto unknown substances of great importance, of which I exhibit magnificent specimens, photographs and lantern slides. Just here, however, I must ask you to make one of the landings from the upper air and permit me to deal with the subject at greater length. You will be astonished at the immense progress which has been made to the general benefit of our industry.

Of the greatest interest are the alloys of iron with other heavy metals and metalloids, *i. e.*, alloyed steel.

Instead of carbon, other elements are employed, which likewise enhance the hardness of steel, but prevent the formation of a crystalline micro-structure liable to cracks and flaws. The most important of these elements is nickel.

The readiness with which nickel forms an alloy with iron has long been common knowledge. Even in Bessemer's days attempts were made in Great Britain to turn out cannons made of steel containing 2 per cent nickel. The experiments were not successful because the nickel obtained at that time contained impurities, such as copper, arsenic and sulphur, so that the steel could not be forged. Thirty years later pure nickel, as we know it today, made successful results possible. The same was the case with chromium, silicon and manganese, and not until these elements were produced pure could successful alloys be manufactured with them, either alone or together with nickel. The chief aim in the manufacture of these alloys is the formation of an amorphous, pliable structure of the steel. This result is attained not only by removing more or less carbon, but, above all, by a certain thermic treatment, namely, by suddenly cooling steel heated to a high temperature, heating again and keeping it at a certain lower temperature. Here you can see two samples of steel; in the one case, the coarse crystallization of the pure carbon steel before it is forged, and in the other, the same steel refined by the thermic treatment. The difference in the micro-structure of the forged carbon steel and that of the forged and thermically treated

nickel steel must also be noted. While carbon steel after forging still shows a crystalline structure with visible cleavage planes of the crystals, the section of nickel steel displays an amorphous structure closely resembling that of welded iron. For comparison sake, a sample of a welded iron fracture is exhibited. It must not be overlooked, however, that nickel and chrome-nickel steels are twice or three times as hard as welded iron. There are also exhibited test pieces of alloyed steel construction parts to be used in the automobile industry. Notwithstanding the high tensile strength of about 90 kilos per square millimeter (*i. e.*, about 55 tons per square inch), no fracture is noticeable, although they are greatly bent.

Aside from these improvements, which are of such great moment for structural steel, the iron alloys have found many new applications.

I merely mention the different nickel alloys for ship-building, electric appliances and for valves. These valuable alloys containing 23 per cent and more nickel, are non-magnetic, and not affected by atmospheric influences; those containing 30 per cent nickel possess great resistance to electricity, while the coefficient of expansion of steel with 45 per cent nickel is only one-twentieth of that of ordinary steel and not greater than that of glass.

It is a very interesting and novel fact that by the thermic treatment alone the micro-structure of the cheaper kinds of unalloyed iron plates and iron shapes is so changed that it becomes three times as resistant to the destructive effect of acids. If alloys of iron with chromium, tungsten, molybdenum and aluminum in certain proportions are thermically treated, this resistance is increased fivefold, as is shown by samples of ordinary carbon steel and chrome-nickel steel which underwent a treatment with dilute sulfuric acid for 56 days.

An alloy of ordinary iron with 5 per cent nickel is an excellent material for withstanding hot caustic soda. Most astonishing properties are displayed by steel alloys containing more than 10 per cent. of chromium and a small addition (2.5 per cent) of molybdenum. Such alloys are manufactured in the form of malleable cast and forged iron pieces by Krupp, according to the patents of Borchers and Monnartz in Aix-la-Chapelle and in the form of rolled tubes by the Mannesmann Röhrenwerken in Remscheid. These alloys are insoluble not only in dilute hydrochloric acid and sulphuric acid, but also in dilute nitric acid, even with the addition of alkali-chlorides, and if they contain about 60 per cent. chromium, 35 per cent iron and 2-3 per cent molybdenum they withstand even boiling aqua regia. You see here samples of this extraordinary steel, after treatment with acids, compared with ordinary steel and cast iron.

It must be especially mentioned that the alloys of iron with chromium, tungsten and molybdenum tempered by a special process invented by two Americans—Taylor and White—find most important uses as quick turning steel for all kinds of tools.

The most recent improvements in the manufacture of steel for tools which must of necessity keep pace in hardness with structural steel have been made by the employment of vanadium. Unfortunately, this metal, whose use is steadily increasing, is still very dear, and the chemists' problem is to produce it more cheaply. If the price could be reduced perceptibly, metallurgists prophesy a great future for this metal, which exercises a very favorable influence on the micro-structure of steel.

Of great importance are those alloys of iron with chromium, tungsten and vanadium which possess a high degree of hardness even at 400°-500° C. They are needed by engineers for the construction of steam turbines and for the embossing and spraying of metal objects heated to redness, a process which has lately found extensive application. Chemists use these kinds of steel whenever chemical reactions are carried out at high temperatures and pressure, *e. g.*, for the synthesis of ammonia according to Haber's process.

The very latest alloy has now been patented and is being manufactured by Krupp for the construction of safety vaults and safes. This steel can neither be drilled nor exploded, nor can it be cut by the oxy-hydrogen flame.

Two samples of steel are exhibited, one of ordinary steel in which great holes have been cut in 5½ minutes by using an oxy-hydrogen flame and in 6 minutes by an oxy-acetylene burner, and a specimen of this new alloy which has remained intact after being treated with the same oxy-hydrogen and oxy-acetylene flames for 1½ hours. Let us hope that on this hard and infusible material the scientific safe-burglar will exercise his noble art in vain.

Of the alloys made with manganese, the manganese steel or hard steel, first produced by Robert Hadfield, because of its great wearing qualities is chiefly used for cast iron parts of disintegrators and rails of electric tramways. On account of its hardness, this steel is not malleable, but it can be bent in the cold state and is thus very safe against breaking. It is therefore of much interest to the chemical industry where, in almost all branches, grinding operations are carried out.

Finally, I wish to refer to alloys of iron and silicon which contain 1.5-2.5 per cent silicon and a high percentage of carbon. This steel is excellently adapted for tools and springs which must stand high strain. Since steel alloys containing much silicon, although brittle and porous, have proved very stable against acids, they are now being used more and more where such a property is of importance.

Alloys with about 4 per cent silicon, but very poor in carbon, are of greater value than the above. Robert Hadfield first pointed out the importance of this alloy, while Krupp, working in connection with Capito and Klein, a firm of fine-plate rollers in the Rhineland, considerably improved it and introduced it for electric purposes. It is employed in large quantities in the form of sheets of 0.35 mm. (1/70 in.) thickness for the

construction of dynamos, alternate-current motors and transformers. In Germany alone, the consumption of this alloy already amounts to 8,000 tons a year. This material has a resistance to electricity 4 or 5 times greater than that of ordinary iron and loses only half as many watts, so that the injurious Foucault currents are reduced to a minimum. The manufacture of transformers has therefore become much cheaper, for the proportion between iron and copper is much more economical. The production of this silicon iron alloy with its very low percentage of carbon, and that of the chrome-nickel steels almost free from carbon, became possible only after silicon and chromium, entirely free from carbon, could be manufactured by electric smelting processes.

Since the electric smelting furnace has come into use in the steel industry, the problem of removing sulphur, which engaged the attention of chemists for so many years, has been solved. It has been found that the electric furnace process produces a slag free from metal, and such a slag is the prime requisite for the complete desulphuring of the steel bath.

Superior to the silicon steel, poor in carbon, in its electric properties the "ideal" metal for electromagnets, is the pure electrolytic iron—first produced by Franz Fischer, of Charlottenburg, and now manufactured by the firm of Langbein-Pfauhauser & Co., Leipzig. Formerly it was impossible to produce it free from hydrogen, consequently it was hard and brittle and was not malleable. Only by electrolyzing at 100°-120° C. and employing an iron salt solution mixed with hygroscopic salts, such as calcium chloride, the iron became free from hydrogen. Its hardness then sinks far below that of silver and gold and is not much greater than that of aluminum. It possesses the valuable property of becoming magnetic more quickly than ordinary iron containing carbon or silicon, and also of again losing its magnetism more readily, thus considerably increasing the efficiency of electro-motors for which it is used. Among the exhibits you will find several objects made of this electrolytic iron; for example, a cathode made from an electrolytic iron plate during 5 days of uninterrupted operation; also plates made by rolling; further a motor which, if constructed of silicon iron, would furnish 0.5 h.p., but being composed of electrolytic iron, though in use for several months without appreciable signs of wear, it now furnishes 1.3 h.p.; in other words, it is 2½ times as efficient.

With all these new materials at our disposal, among which I must also mention copper, with 10 per cent silicon, and copper nickel, we shall surely be able to improve all sorts of chemical apparatus that suffer so much from wear and tear.

After this short invasion of the domain of metallurgy, we shall now turn our attention to the chemical industry proper, first dealing with the manufacture of the heavy inorganic chemicals.

Sulphuric Acid.—The triumphal progress of the contact process for the manufacture of sulphuric acid

in the United States scarcely has its parallel in Germany, where it originated. Platinum, in spite of the fact that its price has increased threefold, is still our principal contact agent. As it is possible to carry out other contact processes with various contact materials, we shall certainly find other agents than platinum available for sulphuric anhydride. It ought therefore to be a fruitful field for research to find cheap substitutes for platinum. In the 20 years that have elapsed since Knietzsch first successfully carried out the contact process, the Americans have increased their output threefold for the same weight of platinum. Nevertheless, the old lead-chamber process still competes with the new method, and the steady improvement of this process and the purity of the resulting acid must be acknowledged. In fact, the lead-chamber process promises to make further progress in the future in view of the success of Falding's high chambers and Opls towers, in which large quantities of acid flow down.

The Gaillard tower is supreme for concentration and recovery of the acid and for the regeneration of the various waste acids.

Ammonium Sulphate.—A new way of manufacturing sulphuric acid, together with ammonia, from the gases which are produced by the dry distillation of coal, is looming above the horizon. Burkheiser is seeking, with the aid of especially prepared wet iron compounds, to bind the sulphur, simultaneously absorbing cyan, and to convert the ammonium sulphite thus produced into ammonium sulphate by oxidation with atmospheric air.

In competition with Burkheiser, Walter Feld is endeavoring to recover sulphur directly as ammonium sulphate by a series of interesting reactions, in which thiosulphates play an important part. Such plants are in operation in Königsberg and here in New York.

Nitrogen Compounds.—So much has been written concerning the progress made in the last 5 years in the utilization of atmospheric nitrogen, that I need not enter into a description of Birkeland-Eyde's, Schönherr's or Pauling's process for the direct oxidation of nitrogen by means of the electrical discharge, nor of Frank-Caro's method of forming a cyanamide from carbides, nor is it necessary to describe the Serpek process for the production of ammonia from aluminum nitrides combined with the utilization of alumina which is simultaneously obtained. I will mention, however, that the problem of concentrating the dilute nitric acid, as obtained in the large absorption apparatus from nitrous gases, has been solved by Pauling's method, in which sulphuric acid is used in a battery of towers. It is also possible now to economically convert cyanamide into ammonia and this again into nitric acid.

Soda and Chlorine.—The 50-year-old Solvay process, which has conquered the whole world, still remains master of the situation. This is all the more remarkable since it is still imperfect as far as the yield

is concerned; a quarter of the salt used in the process is lost as such and the whole amount of chlorine in the form of calcium chloride.

Although the materials employed in the Le Blanc process are completely utilized, this fact will not give it any chance of surviving, and it would seem to be now chiefly of historical interest.

Not less remarkable is the 25 years' career of the alkali-chloride electrolysis. The limited market for chlorine compounds and the great space taken up by the electrolyzing baths were great obstacles to the progress of this apparently simple method. For the same reasons the most approved processes, such as the Griesheim cement cell, the quicksilver cathodes of Castner and his successors, the Aussig Bell and the wire-gauze diaphragm of Hargreaves, with its many varieties, of which the Townsend cell is the latest and best, did not develop as expected. The limited demand also quickly restricted the operation of the brilliant method of manufacturing chlorates by electrolysis.

Tin.—Tin is not only produced from natural ores, but also in more than 20 detinning establishments from tin-plate and tin-can waste; 200,000 tons of tin-plate waste are subjected to this treatment and about 24 million marks (\$6,000,000) worth of tin and iron are recovered. The electrolytic detinning process, on account of high wages, the great cost of current, and the considerable manufacturing loss, has been replaced—where there is a market for chloride of tin—by the patented process of Thomas Goldschmidt, of Essen. The process takes advantage of the properties of chlorine gas, in the dry state, to greedily take up tin without reacting on iron if certain temperatures are observed. Instead of the inferior quality of electrolytic tin mud, which must be converted into marketable tin by costly smelting operations, the new process yields an anhydrous tin chloride used in large quantities for weighting silk. The detinning with chlorine is not carried out with cuttings, as in the electrolytic process, but with waste pressed in hard packages so that 20 times as much material can be treated in the apparatus at the same time. In the United States this process is operated by the Goldschmidt Detinning Company of New York.

Reducing and Oxidizing Agents.—One of the most brilliant successes in applied chemistry has been achieved by the persevering experiments of some chemists with a long neglected substance, the constitution of which had never been properly understood. The old hydrosulphite of Schützenberger, rendered stable and easily transportable in powder form as an anhydrous sodium salt or as Rongalite in combination with formaldehyde, has now become a most important article of commerce. It is chiefly used in vat dyeing and for reducing purposes in general, such as stripping dyed fabrics and as Decrolin for bleaching sugar.

Peroxides, Persulphates and Perborates.—Peroxide of hydrogen and its derivatives at present find less

favor in commerce, although their future appears to be very brilliant. Recently the *Farbenfabriken vorm. Friedrich Bayer & Co.*, succeeded in rendering this important oxidizing agent, which easily decomposes and can be marketed only in water solution, solid and stable by the addition of urea.

This powder is in the market under the name of *Ortizon*, but on account of its relatively high cost is intended not so much for technical as for hygienic and pharmaceutical purposes.

The interesting manufacture of sodium peroxide from sodium and the many scientific investigations of the persalts, have not been followed by great commercial success. The persulphate and perborate, however, the latter under the name of "*Persil*," are being manufactured on a large scale. The reason of this failure seems to be the high cost of production.

Rare Metals.—The most interesting alloys discovered by Muthmann, and Auer have found little application in the arts, and the use of cerium and thorium preparations is still confined to the incandescent gas-light industry. Only the "*Auermetal*," consisting of 35 per cent iron and 65 per cent cerium, is employed, and this only to a limited extent for the manufacture of pocket cigar lighters.

In the metal filament lamp industry, tungsten, which shows the highest melting point of all metals, namely 3100° C., has replaced tantalum, which melts at about 2300° C. This became possible only after successful experiments to render the metal ductile by hammering.

The elements cadmium, selenium and tellurium are obtained in great quantities as by-products; the first is produced in the zinc industry and the other two from the Tellur gold ores found in Cripple Creek, Colorado. Although sold at relatively low prices, they find but little use in the industries.

Artificial Precious Stones.—Finally, I will, in but a few words, touch upon a new industry, *viz.*, the synthetic manufacture of precious stones from alumina with additions of chrome oxide, iron oxide or titanitic acid. Artificial rubies and white, yellow and blue sapphires, which cannot be distinguished from natural stones, are being manufactured in great quantities in Paris and recently also by the *Electrochemische Werke, Bitterfeld*. They are used extensively for jewelry and especially as bearings in watches and measuring instruments.

All this will give you a striking picture of the development of inorganic chemistry which is taking a more and more important position beside organic chemistry.

Applied Organic Chemistry.—In the organic chemical industry the reactions are considerably more complicated and the apparatus mostly smaller than in the inorganic industry. Here the chemist, like a juggler with his balls, gives every atom a definite position in the many thousand combinations which carbon forms with hydrogen, oxygen, nitrogen and sulphur, and

there exist the most varied reactions and processes which may lead to the same result. This chemistry of the carbon compounds has been most wonderfully perfected in the coal-tar color industry, and in every factory of this branch there are hundreds of scientifically trained chemists always experimenting and daily finding new combinations possessing properties of technical value. Before these products become finished articles to be sold as colors, perfumes or pharmaceutical preparations, they must further go through a series of numerous intermediary operations, which finally lead to the marketable chemicals.

Coal-Tar.—The starting material of the important coal-tar industry is the black tar which is obtained by the dry distillation of coal and is known to contain about 150 different chemical products, of which, aside from carboic acid, the aromatic hydrocarbons, benzole and its homologues, toluol and xylol, naphthalene and anthracene, play the greatest part.

More recently carbazol has been isolated from tar on a large scale and has become a most important raw material for the manufacture of the color "*Hydronblue*" by *Leopold Cassella & Co., Frankfort a/M.* *Hydronblue* is a sulphur dyestuff distinguished by its fastness against washing and chlorine. *Acenaphthen*, which also occurs in coal-tar as such, is the starting material of a red vat dye "*Cibanonred*," discovered by the Society of Chemical Industry in Basle. It is to be regretted that hitherto no technical use has been found for phenanthrene, which is also one of the constituents of tar.

Besides carboic acid, its homologues and the various cresols, etc., are being isolated by Dr. F. Raschig in *Ludwigshafen on the Rhine*. These substances are largely employed in the manufacture of explosives and coloring matters.

As long as coal gas is produced for illuminating and heating purposes and as long as coke must be used for the reduction of iron ores, tar will always remain the cheapest raw material for the manufacture of these hydrocarbons. But since it may become necessary in the future—as is already possible today—to use coal in a more rational way, at the same time producing hydrocarbons, the coal-tar color industry need not fear a scarcity of this important raw material, the less so as certain kinds of petroleum, *e. g.*, *Borneo petroleum*, contain large quantities of aromatic hydrocarbons from which the *Rheinische Benzinwerke, in Reisholz near Düsseldorf*, has already isolated toluene in the form of nitrotoluene in a commercial way. If, however, a still greater demand for these hydrocarbons should occur, other methods of obtaining them must be found. We shall then surely succeed in producing them synthetically either directly from the elements carbon and hydrogen or indirectly from carbide of calcium by passing acetylene through glowing tubes—a reaction which was already carried out successfully in the early sixties of the last century by *Berthelot* and recently by *Richard Meyer*. At the present time about

one-quarter of Germany's annual output of coal is converted into coke, *viz.*, 20 per cent for foundry purposes and 4 per cent in gas works, while in England the quantities are 12 per cent and 6 per cent, respectively.

Distillation of Tar.—The point of greatest importance in the distillation of tar is still the separation and isolation, in the cheapest possible way, of the different hydrocarbons in their purest form. The stills have been continually enlarged, those employed today having a capacity of 60,000-80,000 liters (13,000-17,500 gallons). On the other hand, a continuous process, such as is possible in the bituminous coal-tar industry, has not yet been found. A large number of patents have been taken out for apparatus intended to solve this problem, but none of them have proved satisfactory in practice.

Organic Intermediate Products.—The conversion of the aromatic hydrocarbons into intermediate products necessary for the color industry is almost always carried out by treatment with concentrated sulphuric and nitric acid and subsequent reduction of the thus obtained nitro-compound by means of metals or metallic oxides and sulphides. In the production of amines, iron is the principal agent of reduction, while zinc and tin are mostly used in the production of azo-compounds. The electrolytic reduction has not proved useful for these processes.

The methods of producing nitro- and amido-compounds have been very little changed as far as chemical operations are concerned, but with the increase of their production their poisonous properties became more and more apparent and forced manufacturers to modify the processes so that they could be carried out in tightly closed vessels in order to protect the life and health of the workmen.

In Germany legislation has been recently enacted, based on the experience of the individual factories, which lays down rules and regulations for strict observance.

Several trinitro-compounds have been shown to be explosives, and, like trinitrotoluene, are now largely employed as substitutes of picric acid in the manufacture of explosives.

The introduction of oxy-groups into the molecule is mostly brought about by melting sulpho acids with alkalis, and, according to more recent methods, with alkaline earth metals, such as calcium and barium hydrates. Since chlorine, produced electrolytically, is obtainable in unlimited quantities and chemically pure, chlorine substitution derivatives of the hydrocarbons have been employed for all kinds of synthetical purposes. Many of these chlorine derivatives cannot only be converted into oxy-derivatives by melting with alkalis, but, like paranitro-chlorobenzole, they also directly exchange their chlorine for amide group when treated with ammonia or its derivatives. Colors also often change their shade when a halogen atom is introduced into their molecule and acquire more valuable properties. Chlorine has therefore proved exceedingly

useful in the preparation of intermediate products and will undoubtedly become of still greater service in the future.

In the naphthalene series, the method discovered by Bucherer and Lepetit for the conversion of the hydroxyl group into the amido group and *vice versa*, employing sulphurous acid esters, has proved of great practical value. Phosgene, too, is today being more and more employed. Several decades ago it became an important substance for the production of the urea of paramidobenzolazo-salicylic acid, introduced into the market, under the name of "Cottonyellow," as a beautiful yellow cotton color of great fastness to light. Its principal use, however, was for the manufacture of the bright but fugitive triphenylmethane colors. It is now especially used to combine 2 molecules of aromatic compounds with free amido groups, thus producing urea derivatives, and if the starting material is an azo color, the resulting urea derivative is, as a rule, much faster to light than the original color. Imidazol, thiazol and azimido compounds of the most varied kinds are also manufactured and converted into azo colors.

In the series of the aldehydes and carboxylic acids there are no epoch-making discoveries to be recorded. Chemists still start from hydrocarbons chlorinated in the side chain or directly oxidize the homologues of benzole. Kolbe's synthesis of salicylic acid, of which large quantities are used in the color industry, is also applied at an ever-increasing rate for the production of the oxycarboxylic acids. But the direct introduction of the carboxylic group into the benzole molecule, unsubstituted by hydroxyl, is a greatly desired achievement, which, however, has not yet been attained. It is also a matter of greatest importance that in substitution reactions of the aromatic nucleus we should be able to vary at will the ratio of the isomers to be formed.

Besides the biochemical production of ethyl alcohol from wood waste and from the waste liquors of the sulphite cellulose industry, I wish to mention the synthesis of organic compounds by the addition of water to acetylene. In this manner we produce in a simple way acetaldehyde, which can be easily converted into acetic acid, a very important starting material for the manufacture of numerous products.

The steady search for new raw materials and new intermediate products to be utilized in the manufacture of colors has often been crowned with success. We need only to recall the many intermediate products which have been made available for the production of vat dyes and sulphur colors and which have led to the discovery of new substances with most valuable properties. Very often new lines of research are not always based upon preconceived theoretical ideas, but are opened up by mere accident. A keen power of observation, however, is the most necessary equipment of the chemist who aims at success.

Coal-Tar Colors.—In no branch of technical chemistry has such intense work been performed as in that of

the coal-tar industry. The outsider long ago may have thought that so much had been accomplished in this field that nothing more was left to be done. The countless dyestuffs, giving all the colors of the rainbow, might well have given rise to the belief that there was already a surplus. But here the course of events was just as it generally is in life. With growing possessions man's needs and demands also multiply. While people were formerly content to produce with coal-tar colors every possible shade in undreamt-of brightness in the simplest way, they gradually began to make more and more exacting demands as regards fastness. Not only had materials to be dyed a pleasing shade, but they also had to be fast to washing and light. Thus new, alluring problems were submitted to the color chemist, and his indefatigable efforts have already carried him a long way towards the desired end. Strange to say, among the public, you will frequently meet the view that artificial colors do not give fast dyeings. This is a decided error which cannot be too emphatically contradicted. Today we can produce almost any shade with any desired degree of fastness on any kind of material, whether it be wood, cotton, silk or paper. If the dyer does not always produce such shades it is the fault of the trade which does not express its demands forcibly enough. Of course, the dyeing with fast colors entails a somewhat greater expense, which must naturally be borne by the consumer.

Just at this point, before discussing the progress made in the manufacture of fast colors and in order to prevent misunderstanding, I should like to emphasize the fact that the old colors, though not as fast as those more recently discovered and though, perhaps, quite fugitive in some respects, still have a right to exist. It would be quite foolish to dye certain kinds of paper intended to be in use for only a very short time, with colors absolutely fast to light, or to dye cloth never to be washed, with expensive colors fast to washing, or again, to treat lining, which is but slightly exposed to sunlight, in the same way as materials which must be exceedingly fast to light. Everything according to reason. For many purposes, however, the need for shades fast to light or to both light and washing is so great that it must be given every consideration. How mortifying it must be to notice shortly after you have decorated the walls of your home with most beautiful and expensive materials, that the lovely colors daily grow more unsightly, and to see a solitary patch showing up in all its pristine glory amidst a faded background when a picture or other piece of furniture is moved to another place. As it is possible to guard ourselves against such occurrences, we should certainly do so. Today we are able to produce the most beautifully colored wall-coverings, whether of paper or of woven or printed fabrics, to meet every requirement in regard to fastness. This is proved by the large collection of all kinds of woolen and cotton fabrics (after washing and exposure to light) and especially of wall-papers, of carpets, rubber

material and balloon coverings, which the different firms of the German color and dyeing industry have placed at my disposal for exhibition.

If you now inquire how chemists have been able to make such great progress, my only answer is by logical and untiring efforts along well known ways, undaunted by failures and by diligently following any track, however faint, that gave promise of advance.

In every branch of the color industry these methods have led to faster and ever faster dyestuffs, from the multicolored benzidine colors, described as fugitive to light and not stable to washing, to the anthraquinone colors and the indigoid vat dyes. In all these classes we have gradually learned to recognize certain regularities and to accomplish certain results by systematically grouping the components and fixing the position of the substituting groups; thus we have succeeded in increasing the fastness to light of the individual chemical according to a preconceived plan.

Indigoid Colors.—The synthetic production of colors allied to indigo was stimulated by the successful synthesis of indigo which almost entirely displaced natural indigo and called the attention of both chemist and consumer in an increased measure to the advantages of vat-dyeing. The King of Dyestuffs, Indigo, now finds itself in the company of a whole series of other colors, the brome indigos, the thio indigos and alizarine indigos, the shades ranging from blue to red, violet, gray and black. Even the "purple" of the ancients has been reproduced by Paul Friedlaender, who by isolating the dyeing principle found in certain glands of the purple snail living in the Mediterranean, has demonstrated the fact that this natural color is identical with a dibrom-indigo which had been long before produced synthetically. These indigoid colors possess the same, if not better, properties than indigo itself.

Alizarine Colors.—The fastness of the alizarine colors, *e. g.*, alizarine red, used for Turkey red, was well known in ancient times. But, whereas formerly only mordant colors were considered to be fast, and consequently only these were looked for in the anthraquinone group, which led to the discovery of alizarine-orange, -brown, -blue and the alizarine cyanines, Robert E. Schmidt in 1894-1897 succeeded in finding acid-dyeing anthraquinone colors which dye every shade, rivalling the old and well known triphenylmethanes in brightness and simplicity of application and the alizarine mordant colors in their extraordinary fastness to light. I merely mention alizarine-cyanine-green, alizarine-sky-blue, anthraquinone-blue, alizarine-sapphirole, -astrol, -irisol and rubinol. Their fastness to light is so excellent that in the famous "Manufacture Nationale du gobelins" in Paris, they have replaced the older dyestuffs for the dyeing of wool used in the manufacture of gobelins. This means a great deal if it be borne in mind that a square meter of these gobelins for the production of which an operator needs more than a year, costs, on the average, about 6,000 francs.

Indanthrene and Algole Colors.—An entirely new

era began for the alizarine series when René Bohn in 1901, found that his new color, indanthrene, could be used as a vat-dye for cotton. This color can be dyed in its reduced state like indigo, but is far superior to the latter in beauty and brightness of shade, as well as in fastness to washing and light. Indeed, the fastness to light is so great that in this respect it must be termed indestructible.

On account of this phenomenal fastness, indanthrene blue caused chemists to look for other vat colors in the anthraquinone series. Their efforts did not remain unrewarded, and we already possess colors of this class giving every possible shade. The Badische Anilin and Soda Fabrik sell them under the name of "Indanthrene Colors," the Farbenfabriken vorm Friedrich Bayer & Co. under the name "Algole Colors." Chemically most of these vat colors belong to the indanthrene type; some of them are still more complicated nuclear products of the condensation of several anthraquinone molecules; others, again, are di- and tri-anthraquinonylamines. It must also be noted that to the greatest surprise of all experts in this branch, it was discovered in the laboratory of the Farbenfabriken vorm. Friedrich Bayer & Co., that even some of the simplest acyl derivatives (-benzoyl) of the animoanthraquinones are excellent vat colors.

Lake Colors.—We must not leave out of sight the importance of some colors of the aniline group and especially the anthraquinone group for the production of lakes for paints and pigment colors for wall paper. The alumina lake of alizarine, the so-called madder lake, with its fine shade and great fastness to light, is best known. Other alizarine colors also yield valuable alumina lakes; thus, alizarine sapphirole gives a blue lake of excellent fastness to light. But it is not always necessary to precipitate lakes. Some of the difficultly soluble vat colors may be directly employed in a finely-divided form. Thus indanthrene and algole blue already play important roles as substitutes for ultramarine for bluing higher class paper, textiles and even sugar.

The development of the anthracene colors, aside from the tinctorial progress, brought about remarkable results in pure chemical research, for example the peculiar action of boric acid and the catalytic action of quicksilver in the sulphonation processes of anthraquinone.

But in this branch of our science as well there is still much room for development. Many problems remain unsolved and new ones are continually arising. To satisfy the demand of the dyer many dyestuffs must still be synthesized.

The ceaseless efforts of the color chemist will undoubtedly bring us farther and farther along this road, and complaints about the insufficient fastness of dyed materials will be silenced at last. If this goal is to be reached, it is absolutely necessary for the consumer to support the manufacturer, and I take this opportunity to state that in the United States of America

these fast colors are today more generally used, and found recognition and wide-spread application here earlier than in any other country.

Pharmaceutical Chemistry.—I will now deal with the progress and problems of the pharmaceutical industry in the synthetic production of medicinal drugs. This industry is the youngest daughter of the coal-tar industry and it is not long since she celebrated her 25th anniversary. Those, who, like myself, had the good fortune to stand at her cradle when Ludwig Knorr discovered antipyrin, and to guide her first tottering steps at the time phenacetin and sulfonal were brought out, must look back with a joyful heart to this period of splendid growth. Much brilliant work has been accomplished but a vast amount still remains to be done. Here we see chemistry and medicine intimately bound together, the one dependent upon the other and powerless without its aid. What an organization, what boundless intelligence is necessary and what immense energy has to be expended in order to discover a new synthetic remedy and to smooth its path through the obstacles of commerce! First, we need a fully-equipped chemical laboratory, then a pharmacological institute with a staff of men trained in medicine and chemistry, an abundance of animals to experiment upon, and finally—the latest development in this field—a chemo-therapeutic and bacteriological department equipped according to the ideas of Professor Ehrlich; all these must be in close connection with one another. Whatever has been evolved, and after much painstaking effort selected as useful, finds its way into the manufacturing department, there to be elaborate in the most minute details and brought to the highest possible pitch of perfection. Now begins the arduous work of the scientific department! Here the right sponsors must be found, here all prejudices must be brushed aside and an extensive propaganda initiated. Next, a host of clinicians and practitioners must be called into requisition so that what has been evolved in the silent workshop will be conducted on a stanch ship into the wide sea of publicity. And, finally it is the calculating salesman's turn; he must bring in enough to cover all the expenses of the innumerable experiments that have been made, if the new drug, which has swallowed so much money, is to survive and prosper. Truly, all this is a task which only too often is misunderstood and insufficiently appreciated. If, however, a great hit is made—an event almost as rare as the Greek calends—then the envious, the patent- and trademark-violator, and even the smuggler, cling to our heels and seek to rob us of our profits which, taking everything into consideration, are really not large. But despite all this, and though unfortunately opposed by druggists and physicians even today, the pharmaceutical industry serenely pursues its task. For besides certain economic aims, we also have ideals to strive for. We combat systematically the symptoms of disease and are the faithful auxiliaries both of the doctor and the harassed nurse.

The agonizing pains of the patient we allay with narcotics and anesthetics. When sleep flees the couch of suffering, we compel it to return; fever, we banish. We destroy the minute organisms which cause and spread diseases. Thus we add to the store of what is valuable, and perfect what already exists. We also isolate the active principles of various drugs and thus assure exact dosage and freedom from undesirable or even dangerously by-effects.

In the chemical works of Germany pure chemical science receives its dues. In every branch of inorganic, organic and physiological-biological chemistry we are working with an army of scientifically trained men. In synthetic chemistry, brilliant achievements have fallen to our share. Quite recently, Stolz succeeded in building up adrenalin, Decker in making hydrastinin and Emil Fischer and Wilhelm Traube in producing purin bases. All of these are magnificent accomplishments, and many of them have been effected in the laboratories of the industry.

That even yet, as at the beginning—the antifebrin period—we must trust to chance is shown by the discovery of atophan, the latest valuable antiarthritic, which is due to a fortunate accidental observation. In the subject of the old ergot problem, research work is gradually bringing more light and makes the possibility of synthetically producing a substitute a thing of the near future. The publications on this subject show that hemostatic alkaloids possess a comparatively simple constitution. That sedatives have their place in an age when nervous disorders are so common is not to be wondered at. I need merely remind you of the new adalin which has proved exceedingly useful. Recently, Emil Fischer, the master of chemical research, to whom the pharmaceutical industry is indebted for the synthetic purin bases, *viz.*, caffein, theobromine, and theocin, as well as the valued remedies, veronal and sajodin, has succeeded, after long and fruitless labors, in elucidating the constitution of tannin and producing it synthetically. He has thus proved that it might be possible to manufacture tanning agents of all kinds artificially and has opened up a new and promising field for research.

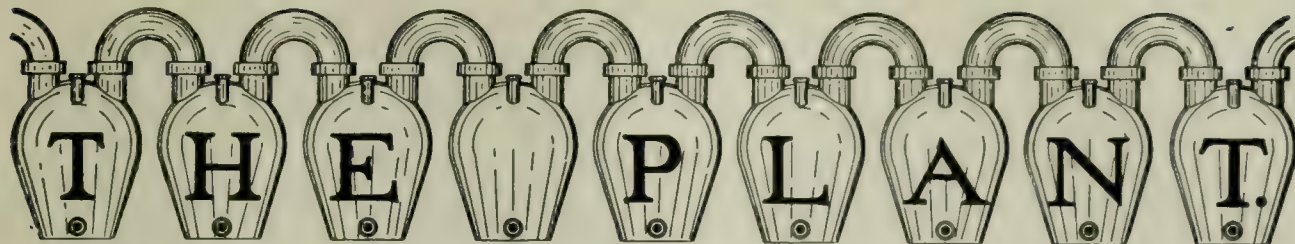
Chemoterapy.—But a short while ago, Ehrlich drew attention to another promising branch of pharmaceutical-medical chemistry, *viz.*, the treatment of infectious diseases by chemical means. After many years' arduous labor and many thousand experiments on different animals, this master of medicine and chemistry succeeded in demonstrating that it is possible to produce chemical substances which will kill the parasites in the human body without injuring their host and that this action is a function of the chemical constitution. The new science, with its magical bullets directed only against the injurious organisms in the body but not affecting its cells, pursued its course from aminophenyl-arsenic acid (atoxyl) to diamino-oxyarsenobenzole (salvarsan). Thus a new synthetic preparation, an arsenic compound, is added to the old and

highly effective remedies, mercury, quinine and salicylic acid. It is certain that we are here only at the beginning of a new development. We know already that we are able to combat not only spirochetes but also bacterial diseases, like tuberculosis. Even carcinoma and sarcoma, those growths so destructive to humanity whose cause is, however, not yet understood, can probably be influenced in a like manner by means of selenium compounds, as first pointed out by Emil Fischer. But were we to learn to cure diseases due to trypanosomes and plasmodia, what a great work we should have accomplished in the interest of humanity and social economy, for it is in the most fruitful lands indeed that these diseases, malaria and sleeping sickness, are to be found, and man and beast are ruthlessly destroyed by them. Neither salvarsan nor atoxyl are of service here, and therefore other hitherto unknown remedies must be found.

While the treatment of syphilis, with its terrible consequences, is still imperfect in spite of mercury and salvarsan, let us hope that systematic laboratory experiments with the innumerable products chemistry is able to produce from mercury and from arsenic will finally lead to complete success.

Synthetic Perfumes.—In the perfume industry the developments made since the scent of the violet was imitated with jonon, and since the successful synthesis of camphor from turpentine, are not of such nature that we need to deal with them at great length. The importance of this industry appears from its yearly turnover of 45-50 million Marks (10-12 million dollars). Here the efforts of the chemists are directed towards determining the constitution of the complex and simple natural perfumes, isolating the various products of decomposition obtained during the investigation, and finally reproducing the natural perfumes synthetically. Such results have already been achieved in the case of the odor of the rose, lily-of-the-valley and violet. Very often certain substances are needed in the compounding of perfumes which, like indole, possess anything but a pleasant smell.

Artificial Silk.—Even if doubt is expressed as to whether artificial silk (the yearly consumption of which amounts to about 7 million kilograms) still belongs to the chemical industry because it stands in such close relation to the textile industry, with its weaving and spinning machines, yet the raw materials needed for its production, such as nitro-cellulose, copper ammonia cellulose and cellulose-xanthogenate are of such importance that the chemist and engineer equally divided the responsibility in this branch of manufacture. Viscose silk from xanthogenate of cellulose, the production of which has been recently very much improved, seems to replace nitro-cellulose silk and the copper ammonia silk. This viscose silk surpasses all other artificial silks in luster and is the cheapest to manufacture, so that the apparently simplest process of all, the copper ammonia cellulose silk, cannot compete with it any more.



SOME ASPECTS OF THE RESIN AND WOOD-PULP INDUSTRIES.

As many chemists in this country are directly concerned with the technical problems of either the resin industry or the woodpulp industry, the following description from *The Chemical World* of some of the problems now in course of solution should prove of interest:

So far as the rise in wood cellulose is concerned, we may content ourselves with the reflection that the causes are largely temporary, depending chiefly on the cycle of good trade following the period of depression which reached its lowest point in 1908. So far as the increase in consumption is permanent, we may rest assured that it can be met and will be met by an extension of the sources of supply in one direction or another. But in the case of resin the commercial position is a very different one; the area of production is extremely limited, the methods of collection have for a long time been crude, wasteful and destructive, and the increase in consumption tends to be permanent and progressive. This position has been largely brought about by the appreciation in the value of vegetable fats by improved methods of refining for edible purposes, so that the buttermaker draws on the materials of the soapmaker, and the latter in his turn bids against the papermaker.

For an account of the resin and turpentine industry we cannot do better than refer to Professor Vèzes, of Bordeaux, who has done much to improve the conditions of the industry in France, and the following information is taken from a *brochure* published by him in 1909. The French turpentine industry is confined to a triangular district called the "Landes," about 3,500,000 acres in extent, with Bordeaux as its principal town. About half this area, 1,750,000 acres, is forest planted with the maritime pine, and the yield of crude turpentine is about 100,000 tons annually. In the United States, forests of long-leaf pine (*P. palustris*) and of certain other varieties occupy a strip about 125 miles wide along the coast of the Atlantic and Gulf of Mexico, extending on both sides of Florida to Virginia in the north and Texas in the west. The forest districts represent about 70,000,000 acres, a considerable portion of which has already been denuded by destructive exploitation. The annual production of the American forests is about 500,000 tons of crude turpentine. Until comparatively recently, these two countries were the only sources of resin products in the world, but small areas in other parts, notably Spain and Portugal, now account for possibly some 30,000 tons more.

The crude oleoresin, the "*gemme*" as it is called in the Landes, exudes in the warm season (from March to October) from an incision made in the trunk. Kept open by the removal of a thin slice every week, this incision—the "*carre*"—rises gradually up the trunk until it reaches, after five years' working, a height of four yards or so. The tree is then left to recover for two or three years, after which time a fresh *carre* is made at another point of the base. The tree is thus tapped for about forty years, after which it is "bled to death" (several *carres* being worked simultaneously) before being felled for lumber purposes. In the Landes district strict arrangements are carried out for replanting the forest, so that the resin production of the district is maintained. In the United States this conservative system has not been followed, it having been the custom to tap the trees "to death" from the beginning, and every plot which was subjected to tapping was practically destroyed after four years' working, without any systematic steps being taken to ensure its re-establishment. Recently, however, this wholesale denudation has attracted public attention, and a better system of exploitation may be expected to result.

From the top of the *carre* the drops of *gemme*, as they exude from the resin ducts of the tree, run down into a receiver. In France, in former times, and in America, until quite recently, the receiver was merely a hole hollowed out of the trunk at the base of the *carre*. The irrationality of this method has, however, been recognized, and the general procedure now is to hang an earthenware or metal pot below the point where the resin is exuding. The contents of the pots are transferred about once a month into casks which, when filled, are taken to the distilleries. There the *gemme* undergoes two processes: First, a fusion for the separation of the oleoresin from the water and dirt, and secondly, a distillation in presence of steam for the manufacture of the two commercial products—volatile oil of turpentine and non-volatile resin (rosin or colophony). The relative proportions of products of Bordeaux turpentine are 20 per cent of oil, 70 per cent of resin and 10 per cent of water and dirt.

Professor Vèzes has done much good work toward improving the quality of the products, not only in connection with the distillation, but also in connection with the collection of the crude material. It is recognized that the resin, both crude and in the course of manufacture, is a substance extremely sensitive to the oxidizing action of air and sunlight. This action adversely affects both the color of the product and its physical properties. A great improvement has been

effected by reducing the period of exposure of the *gemme* during its stay in the incision, by raising the pot which receives the exudate at frequent intervals, so that the path traversed in its flow is as far as possible restricted, and by collecting the contents of the ports more frequently. By these alterations both the loss by evaporation of the oil and the coloration of the resin by oxidation are materially reduced.

Turning now to the conditions of the industry as it exists in the south of the U. S. A., some extremely valuable information is to be found in a paper by G. Walker on the utilization of wood waste (*Jour. Soc. Chem. Ind.*, 1911, 934). According to this authority, some 1,500,000 acres of virgin forest are destroyed annually after the trees have been tapped for turpentine over a period of four or five years. In the absence of organized lumbering arrangements most of the exhausted trees are left until they fall. The bark and sapwood decay in from five to ten years, leaving a resinous heart, which is termed "light wood," because it burns with a luminous flame suitable for lighting purposes. This "light wood" is extremely rich in resin, sometimes containing as much as 40 per cent, and it would appear that the resinous matter by some natural process concentrates in the heart of the tree after it is apparently dead. To some extent this "light wood" is utilized for the manufacture of gas, solvent oils and heavy oils by destructive distillation, but the author indicates that a far more rational method of exploiting it is to recover the valuable oil of turpentine and resin as such and to convert the residual wood into cellulose pulp.

The first portion of this double proposition is actually being carried out on a commercial scale at Conway, South Carolina, under the author's direction. The resinous "light wood," reduced to a fine state of division, is subjected to the action of live steam in steel cylinders for the distillation of the oil of turpentine and pine oil, and the residual wood is then treated with a volatile solvent for the extraction of the non-volatile resin. This apparatus is now producing resin at the rate of 200 barrels a week, and it is stated that five times as much resin and turpentine are obtained in twelve hours as are produced by the same amount of wood in four or five years by the tapping method. The author foresees, in conjunction with an organized system of forest conservation, the resin industry of the future worked in combination with the manufacture of woodpulp. The old wasteful system of tapping will die out, and the trees on reaching maturity (about twenty-five years' growth) will be felled full of resin.

In his projected scheme the author still appears to contemplate the rotting away of the exterior sapwood in order to operate on the highly resinous "light wood," a process requiring five to ten years. There may be reasons, unstated, for this apparently wasteful complication, possibly connected with the expense of treating with solvents any but the richest portion of the

trees; that, however, is a detail which may be trusted to solve itself on its economic merits, taking into account the yield of cellulose to be obtained from the fresh sapwood. The extraction of resin by volatile solvents and the manufacture of woodpulp, it is interesting to note, possess two technical features in common, viz., the necessity of first eliminating the colored external layers of bark which would degrade the color of the resin extracted by the solvent and contaminate the purity of the cellulose; and secondly, the necessity of reducing the wood to chips of small dimensions before subjecting it to treatment.

Another worker in the same field, who has arrived at identical conclusions, is G. B. Frankforter, who has successfully carried out on an experimental scale the extraction of the oleoresin and the manufacture of cellulose from the same wood. An account of his work is given in the *Jour. Ind. and Eng. Chem.*, 1911, 3, 4—10. Two practical difficulties suggest themselves in the extraction of large quantities of a bulky material with hydrocarbon solvents as outlined by Walker. One is the difficulty of penetrating with the hydrocarbon a material which is already wetted in the preliminary steaming off of the volatile oil of turpentine by saturated steam. The other is the large amount of hydrocarbon solvent which must be carried through the apparatus and continuously redistilled in performing the operation on an industrial scale. The first difficulty might conceivably be met by keeping the chips sufficiently dry during the distillation of the volatile oil by using superheated steam. Frankforter, however, adopts the method of taking out the volatile oil and the resin together by means of the solvent, leaving the treatment of the oleoresin for a subsequent operation. The solvent employed is petroleum spirit or coke-oven benzene, and the chips of resinous wood are charged into a battery of extraction vessels of sufficient size and strength to serve as digesters for the ultimate conversion of the exhausted chips into cellulose by the caustic soda or sulphate of soda process. The amount of solvent required for the extraction of the resin is very considerably curtailed by performing the extraction by means of the vapor of the hydrocarbon. Instead of filling the digesters with the liquid solvent as in the ordinary method of extraction, the hydrocarbon is first volatilized in a steam-heated boiler and the vapors only are passed through the chips, condensing on them and liquifying the oleoresin contained therein, so that it runs down into the still in the form of a concentrated solution. This modification must largely diminish the cost of the treatment and go far to bring it within the range of a practical industry. The subsequent operations are simple: the exhausted chips are steamed in order to recover the solvent remaining in them, and the caustic lye is then admitted into the same vessel, so that conversion into cellulose follows in the ordinary way by cooking under pressure without disturbing the charge of wood.

The waste of wood which takes place in the America resin forests, large though it is, is only a fraction of the total waste which takes place in connection with the whole lumber industry; but the general problem of waste wood utilization is considerably more complicated, and the prospective results of its solution are less obviously remunerative than in the case of the particular aspect here discussed. Enough has been said to indicate that with efficient organization and scientific co-operation the stringent outlook for the world's supply of resin products might be considerably alleviated, and natural resources which are now being merely frittered away by methods excusable in a new territory might be developed in a spirit worthy of a great industrial nation.

SOME FACTORS IN THE COST OF SODIUM HYPOCHLORITE PRODUCTION.*

By W. H. WALKER and R. F. GEGENHEIMER.

In the manufacture of bleaching liquor, or sodium hypochlorite, by the direct electrolysis of common salt, the four more important factors entering into the final cost are labor, deterioration of apparatus, cost of salt consumed, and cost of power employed. Of these, the first two, while important, are not subject to the variation incident to change in locality of the operation as are the last two, and are relatively constant. It is therefore to the relation of the cost of salt and cost of power as influenced by the conditions under which an apparatus may be operated that the paper read by the authors before the Eighth International Congress of Applied Chemistry was devoted. The experimental data employed were obtained from experiments made with an electrolyzing apparatus of the continuous flow type, which consisted of a rectangular trough divided into twenty-four compartments by bipolar electrodes of graphite. The salt solution to be decomposed was fed continuously into one end of the apparatus, passed successively between each pair of electrodes, and excited at the opposite end. The electric current was supplied from a 110-volt lighting circuit, the amperes flowing depending upon the total resistance of the apparatus.

Since the salt solution as made up is used in its entirety for bleaching purposes, however much or little of the salt therein contained may have been converted into the active bleaching agent, sodium hypochlorite (in any case there being always a large excess of unconverted salt), it is obvious that the less salt the solution contains per gallon, the cheaper the resultant bleach solution will be. From this point of view, therefore, the apparatus should be fed with as dilute a solution of salt as will conduct the electric current through it. But, on the other hand, the more dilute the salt solution is—that is, the less salt it contains per gallon—the more electrical power will be required to

form a given amount of sodium hypochlorite in it. It becomes important, therefore, to consider the relationship which exists between the strength of salt solution used and the factors controlling the amount of electrical energy consumed per unit of sodium hypochlorite produced.

It can be shown that the cost of bleaching solution as measured by the cost of salt and electrical power consumed is influenced by a large number of factors, and that not infrequently the maintenance of one condition will influence the cost in opposite ways. Summing up these factors, their relationship may be expressed in a general way as follows:

That increasing the amount of salt per gallon of salt solution used increases the total cost because it (1) makes more expensive the first cost of the solution; (2) causes a higher final temperature with heavy chlorate formation; (3) it increases the amount of current flowing, and increases deterioration of electrodes.

It decreases the cost because it (1) lowers the resistance to the current and consumes less energy; (2) decreases chlorate formation at the anode; (3) increases production of cell.

A rapid rate of flow of solution increases the final cost because it (1) increases the consumption of salt.

It decreases the cost because (1) it maintains a lower temperature and prevents chlorate loss; (2) it maintains a lower hypochlorite concentration and prevents reduction at the cathode; (3) it lowers chlorate formation at the anode.

Increasing the amount of available chlorine per gallon of solution increases the final cost because it (1) increases the reduction loss of the cathode; (2) increases the oxidation loss at the cathode; (3) increases the temperature of outflowing solution.

But it greatly decreases the total cost because it (1) makes more available chlorine per gallon effluent, and hence reduces the number of gallons of solution required for a determined amount of available chlorine.

It is apparent from the above considerations that if a large amount of salt is used, economies will be effected in electric power and *vice versa*. The price which must be paid for salt and power varies at different localities, and the amount of salt and power which is most economical at one place may be the wrong amount to use at another place where the costs are different. The question arises, therefore, how can the relationship between the cost of salt and cost of power be established, and how can such relationships be most conveniently expressed in order to be of general use?

Obviously, from the complicated relationship shown above, it will be necessary to make a great many experiments if the variations in the several factors affecting the result are to be shown in a quantitative way. The following method was therefore developed, by which, from the data from one experiment, a series of results may be calculated.

The apparatus was equipped with thermometers and

*From the Chemical Trade Journal and Chemical Engineer.

means of withdrawing samples for analysis in the 4th, 8th, 12th, 16th, 18th, 22nd and end compartments. The run was commenced with a definite strength of salt solution, and the rate of flow was fixed as would give a strong bleaching solution in the last compartment. The current was allowed to flow for an hour or so, or until the apparatus came to equilibrium—that is, until the flow of current and the flow of solution into and out of the apparatus were constant, the temperature of the different compartments did not change and the strength of available chlorine in the last compartment was constant. At this point the temperature in each cell was read, and a sample of the solution was taken from each of the cells equipped for the purpose—that is, 4, 8, 12, etc.

This sample represents the condition of the solution which would obtain if the apparatus ended with the respective compartments. That is supposing the apparatus ended with the fourth compartment, then the solution would leave at this point and would have the temperature and composition of the sample taken from the compartment, when the current and rate of flow were as above given. This is true of the other compartments tested.

The complete data for such a run are given:

Run No. 20.

Sp. gr. salt solution at 15° C., 1.0335 = 0.4 lb. per gallon.

Average voltage, 104.

Average current, 39 amperes.

Rate of flow, 11.5 gals. per hour.

Cost of salt per pound, .5 cent.

Cost of power per K. W. H., 2 cents.

Temperature inlet solution, 53.6° F.

Temperature outlet solution, 125.6° F.

Temperature rise, 72° F.

TABLE I.

No. cell.	Temp. ° F.	Lbs. Cl. per gal.	Current eff- ciency: %	K. W. H. per lb. Cl.	Lbs. salt per lb. Cl.	Cost power.	Cost salt.	Combined salt and power per lb. avail. Cl.
4	69.8	0.0178	60.5	2.44	22.5	0.0488	0.1125	0.1613
8	80.6	0.0294	50.2	2.94	13.6	0.0588	0.0680	0.1268
12	95.0	0.0418	47.5	3.11	9.57	0.0622	0.0479	0.1101
16	107.6	0.0492	41.9	3.52	8.14	0.0704	0.0407	0.1111
18	114.8	0.0529	38.0	3.88	7.56	0.0776	0.0378	0.1154
22	125.6	0.0563	34.9	4.23	7.12	0.0846	0.0356	0.1202
End	126.5	0.0574	32.6	4.52	6.97	0.0904	0.0349	0.1253

Table I shows in the second column how the temperature of the solution increased as it passed through the apparatus; the third indicates the way in which the available chlorine is increased in pounds per gallon. The fourth column gives the percentage of the current passing through, which has been utilized in making the desired product, and it is seen to fall off as the end of the apparatus is reached. The power consumed per pound of available chlorine produced therefrom increases, while the amount of salt used per pound of available chlorine decreases as the solution becomes stronger in its bleaching power. This is true also of the cost of the two elements.

Following the explanation given above, it will be seen that if the apparatus ended with the fourth compartment, and was fed with salt solution containing 0.4 lb. per gallon, at the rate of 11.5 gals. per hour, a current of 29 amperes would pass through, and the outflowing bleach liquor would be at a temperature of 69.8° F., and would contain 0.0178 lb. of available chlorine per gallon. The current efficiency would be 60.5 per cent, and the total cost per pound of available chlorine provided would be 0.1613 cent. If the apparatus ended with the twelfth compartment, the table shows the values which would here be obtained, and so on.

It is seen, therefore, that under the condition of cost of salt and power, strength of salt solution and rate of flow, as here obtaining, it would be cheapest to stop the operation at the twelfth compartment, where the available chlorine produced cost 0.1101 cent per lb. Beyond this point, as the solution passes through the apparatus more hypochlorite is formed; but the expenditure for power is so large owing to chlorate formation and cathode reduction as compared with the saving in salt, that the net cost of available chlorine produced becomes larger as the operation goes beyond the twelfth compartment.

But since the apparatus is of twenty-four compartments designed to operate on a current of 110 volts, in order to use an apparatus of the size represented by the twelfth compartment a generator furnishing twelve twenty-fourths of 110 volts, or 55 volts, would be required. Since the current is limited to 110 volts, the question arises how can the conditions be varied so as to have the entire apparatus operate so that the yield of available chlorine, current efficiency, and cost of materials will be the same at the end of the twenty-fourth compartment as it was in the experiment at the twelfth compartment, or at any other selected compartment? The answer may be found in the following considerations:

Let it be assumed that in an experiment as above described it was found that available chlorine was produced at the lowest price in the twelfth compartment. It would be impossible to allow the apparatus to empty at this point and pass the current through but twelve compartments, because the voltage of the line being 110, the resistance would be half too low in but twelve compartments and twice too much current would pass. An external resistance of any form equivalent to 55 volts could be inserted, but the energy consumed by such resistance is total waste, so far as making available chlorine is concerned. Instead of a resistance of 55 volts, however, another apparatus exactly like the first twelve-compartment one can be put in, and the current at 110 volts as furnished from the line be used. This apparatus would be fed with the same strength brine at the same rate, and the result would be that the same results of minimum cost in both pieces of apparatus would be obtained, the entire energy of the line would be used, and twice as

many gallons of bleaching solution would be produced.

Now, practically, this same result may be accomplished if the original apparatus with the 110 volt current is used, and the salt solution run through twice as fast as in the experimental run. While the additional rate of flow would, of course, maintain a lower temperature, and hence a smaller number of amperes would flow through the apparatus, the loss of hypochlorite through the reduction would be greater, inasmuch as that made in the first compartment is subjected to the cathodes of the following compartments, and the concentration of the hypochlorite would also increase more slowly, and consequently the loss would be correspondingly smaller. Hence if by such a run it is found that available chlorine can be produced cheaper after the solution has passed through any given number of compartments, N, at the rate of flow of R gallons per minute, the rate X at which the solution must flow through the entire twenty-four compartments of the apparatus to get the same cost per pound is given by the proportion:

N.	24.	R.	X.
The number of compartments in experimental run giving minimum cost.	The entire apparatus.	The rate of flow during experimental run.	The required rate of flow through entire apparatus.

To test the validity of this method, two runs were made with a 5 per cent brine, on one at the rate of 35 litres per hour, and another at 70 litres per hour. According to the above reasoning, the results obtained at cell No. 12 in the first run should be the same within the limits of experimental error as the results at the end of the apparatus when the rate is twice as fast. The values given in table on next column were obtained.

The figures show a satisfactory check on the method.

The combined cost of salt and power may be expressed as a ratio of one to the other. Thus, if the cost of power per K.W.H. is 2 cents, and the cost of salt is 0.5 cent per pound, the ratio is 2 divided by 0.5 or four. That is, power is four times as expensive as salt in their respective units. By taking these figures

	Results at compartment No. 12.	Results at end of apparatus.
Rate of flow—litres per hour.....	35	70
Grammes chlorine per litre.....	3.7	3.8
Temperature rise	15° C.	15° C.
Current efficiency	45.6 per cent.	46.8 per cent.
Cost per kilogramme chlorine.....	\$0.270	\$0.271

as unity, a table may be constructed showing the relation between the rate of flow of any given brine through the apparatus, and the combined cost at any ratio of cost of salt to cost of power.

Exports of plantation rubber from the Federated Malay States during October aggregated 3,210,831 lbs., making the total shipments for ten months of the year 27,912,613 lbs., against 15,443,154 lbs. in the corresponding period of 1911.

NEW TREATMENT FOR PAPER MATERIAL.*

Ludwig Herz, of Nuremberg, Germany, is the inventor of certain improvements in processes for treating vegetable and textile fiber, waste paper, wood waste and the like for conversion into paper material, for which he has obtained patent rights.

The invention relates to a process by the employment of which vegetable and textile fiber, waste paper and wood can be rapidly and by cold treatment converted into a bleachable paper material.

According to the patent specifications the material to be treated is first soaked in a receptacle filled with a solution of caustic soda and water and then passed between press rollers into a churn or centrifugal machine. Any larger bodies or fibers remaining in the mass are crushed by the rollers before entering the centrifugal machine; in the latter the mass is then churned by suitable beaters in order to loosen it and gradually washed by the passage of water, which removes the soda and all substances not necessary for papermaking. The resulting mass is now ready for further engine or hand treatment and may, if necessary, be bleached in known manner.

During the treatment of the mass in the churn or centrifugal machine, fresh material is introduced into the soaking receptacle, which will be sufficiently soaked by the time the first lot is churned and washed, so that work can be continued without interruption.

If the soaking requires a greater length of time than the churning and washing, it will be advisable to provide two or more soaking receptacles for each churn, so that the work can be continued without interruption.

If necessary, the mass may be passed between rollers a second time in the centrifugal machine.

For treatment by the process the following materials are, for instance, suitable: grass-wrack, forest hay, reeds, maize and sugar-cane, jute, asparagus stalks and all other cheap vegetable substances having a fibrous structure; further, rags and waste paper of any kind and in any condition. For instance, the rags may be oily or greasy, and the paper may be colored, printed on, or written on.

As soaking solution the following has been found suitable: 8 grams of caustic soda to 1 liter of water, to which may be added 0.01 liter of aqua ammonia to prevent a possible crystallization of the soda.

Hard and tough materials may be soaked for several hours in this solution. The churning and washing in the centrifugal machine will, however, be accomplished in a much shorter space of time.

It must be mentioned that most of the above mentioned materials can only be bleached after treatment according to the present invention.

In the soaking receptacle rotating arms for stirring the mass may also be provided, in order to keep the

*From Paper.

mass in constant movement and to begin the work of disintegration.

If desired, the soda contained in the liquid leaving the centrifugal machine may be by suitable treatment again regained.

The material, resulting from the process here described is very suitable as an insulating medium, for instance, instead of cork. For this purpose, the mass remaining in the centrifuge is taken out, mixed with chromic acid and size and then pressed. A good proportion is: 200 kilograms of the mass, 0.5 kilograms of chemically pure chromic acid and 4 kilograms of size.

It must further be mentioned that this process may also be used for cleaning linen or wool waste and the like. For this purpose, the materials to be cleaned are placed in the above-mentioned soaking solution for a suitable period and then washed until all traces of soda are removed. Also here it will be found advisable to soak the material under treatment in one receptacle and then to remove the soda in a second receptacle and to keep the material in constant movement by means of rotating arms in both receptacles.

The inventor makes the following claims:

1. The process for treating vegetable and textile fiber, waste paper, wood waste and the like for conversion into paper material, which consists in soaking the material to be treated in a solution of caustic soda in water in the cold state, said solution containing ammonia in the substantial proportions of 8 grams of caustic soda and .01 liter of aqua ammonia to each liter of water and at the same time starting the disintegration of the fibers while being so treated, pressing the mass so as to crush the solid material, then subjecting the mass to centrifugal action and at the same time washing and churning the material, subjecting the mass to further pressure while being churned and subjected to centrifugal action, and then subjecting the resulting material to treatment with chromic acid and size, the operations being conducted with the materials in the cold state.

2. The process for treating vegetable and textile fiber, waste paper, wood waste and the like for conversion into paper material, which consists in soaking the material to be treated in a solution of caustic soda in water containing ammonia in the cold state and at the same time starting disintegration of the material while being so treated, passing the mass between rollers whereby the solid material is crushed, then subjecting the mass to centrifugal action and at the same time churning and washing the same whereby caustic soda is removed from the material, subjecting the mass to further pressure while being churned and subjected to centrifugal action, and then subjecting the resulting material to treatment with a mixture of chromic acid.

An experimental crop of Egyptian cotton has been raised near Phoenix, Ariz. The crop amounts to about 450 bales and will be sold at about 23 cents per pound.

NEW SOURCES FOR WOOD OIL.

New sources for the supplying of wood oil to American paint manufacturers may be opened up within the territory of the United States if the experiments at present being carried on by the United States Department of Agriculture prove successful. Wood oil is produced from the nuts of the "tungshu" tree (*Aleurites fordii*) of China, and at present practically the entire supply comes from that country. The normal price of this oil is 60 cents per gallon, and in the fiscal year ended June 30, 1911, the United States imported 5,000,000 gallons.

It is known that the wood oil tree will grow along the Pacific Coast south of Sacramento and in the Gulf States, possibly up into Georgia and South Carolina. As yet, however, there are no groves of these trees in the United States from which data as to the possibility of producing this oil in commercial quantities in this country can be obtained.

Another possible source of supply is opened by the work of Dr. E. V. Wilcox, director of the United States Department of Agriculture's experiment station in Hawaii, who is investigating the percentage of oil obtainable from the kukui nut (*Aleurites moluccana*, or candlenut), which grows abundantly in Hawaii and the Philippines. These nuts yield an oil having the same properties and uses as wood oil, which was formerly exported in large quantities. If the nuts can be gathered and the oil extracted profitably this oil should compete in the American market with Chinese wood oil. It is proposed to employ children and old people to gather the nuts, a method which has proved very successful in Hawaii in obtaining supplies of algaroba beans for the manufacture of foodstuffs.

The production of anthracite in Pennsylvania includes an appreciable quantity of usable fuel recovered from the old culm banks by washeries, and the unsightly monuments to the wasteful methods of early times are disappearing from the landscape in the anthracite region. The quantity of coal recovered in the 22 years since the first washery was constructed in 1890 has amounted to about 50,000,000 long tons, considerably more than the total production of anthracite at the beginning of the period. In 1911 the washery product amounted to 4,136,044 long tons. In addition to the coal recovered from the culm banks, 94,647 long tons in 1911, and 91,833 tons in 1910, were recovered from the bottom of Susquehanna River by dredges.

In the bituminous regions the principal use of washeries is to improve the quality of the slack coal used in the manufacture of coke by reducing the ash and sulphur, although considerable quantities, particularly in Illinois, are washed in the preparation of sized coal for household use. The quantity of bituminous coal washed at the mines in 1911 was 12,543,114 short tons. The washeries yielded 10,999,481 tons of cleaned coal and 1,543,633 tons of refuse.

THE LABORATORY

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

The Determination of Carbon in Iron and Steel.

At the Armour Institute of Technology the students in the Course of Chemical Engineering study the Metallurgy of Iron and Steel throughout the Junior year. Two hours a week are devoted to lectures on the subject and four hours a week, or one afternoon each week, is assigned to laboratory work or excursions to metallurgical plants.

An important part of this laboratory work consists in the analysis of iron and steel. The determinations

The combustion is made in a silica tube heated to $1,000^{\circ}\text{C}.$; the oxygen from the gas receiver is purified by passing through wash bottles containing liquid potassium hydroxide, solid potassium hydroxide and calcium chloride, respectively. The silica tube is heated in an electric resistance furnace; the furnace requires 6 amperes at 110 volts and needs about an hour to acquire a temperature of $1,000^{\circ}\text{C}.$ The silica tube contains a wad of platinum gauze just beyond the boat. Directly connected to the combustion tube is a U-tube containing granular zinc, then a tube containing calcium chloride and finally the absorption bulbs. The absorption bulbs must contain fresh potassium hydroxide and the little calcium chloride tube with the bulbs must also be filled with fresh material. All



Fig. 1.—Arrangement of Apparatus for Determination of Carbon.

are for silicon, manganese, phosphorus, sulphur, total carbon, graphite, color carbon and nickel.

After trying out the methods for total carbon and graphite by the use of the standard gas combustion furnace, the Shimer crucible, the method of de Nolly and the electric tube furnace the latter has been adopted as the most suitable for student use.

One furnace and the oxygen receiver appear in the illustration, Fig. 1. Each student is allowed one laboratory period to make his duplicate runs on both total and graphitic carbon. Sometimes two students get their work satisfactorily completed with one furnace during the four hours. Each student receives copies of the two following instruction sheets several days before the assignment:

Total Carbon.—The sample should be as finely divided as possible.

Two grams of the sample are weighed out into the alundum boat which has been previously partly filled with the purest granular alundum.

The weight of the absorption bulbs is taken at the same time the samples are weighed out.

connections must be gas tight and the temperature fully attained and every piece completely filled with oxygen before cutting out and weighing the bulbs for the first determination. A platinum cover keeps the burning oxide from spattering.

The run is made by first connecting the weighed absorption bulbs and opening a free passage through all the absorption apparatus. The stopper is then removed at the tank end of the silica tube and the boat slipped in the required distance, replacing the stopper as quickly as possible and admitting oxygen from the tank. The oxygen is then regulated to a steady and brisk bubbling of the gas through the bulbs for 15 minutes, when the bulbs are disconnected and weighed.

Graphite.—Weigh 2 grams of the substance into a 150 cc. beaker and dissolve in 30 cc. nitric acid, sp. gr. 1.20. A few drops of hydrofluoric acid may be added to remove silica. Bring to boiling and filter into a platinum boat or an ordinary Gooch which has been made ready with ignited asbestos.

Wash the graphite in the boat or crucible with hot

dilute hydrochloric acid, then with hot caustic potash solution, sp. gr. 1.2, and finally with hot water. Dry in oven at 100° C.

If the boat has been used it may be laid in the alundum boat and the determination completed as for total carbon; if the Gooch is used the dried graphite must be transferred to the alundum boat, when the rest of the determination is made as before.

Notes on the Determination of carbon in iron and steel.—Atomic weight of carbon, 12.00 (oxygen, 16.0).

Condition of Carbon: Graphite, amorphous carbon, cementite, free, eutectic, eutectoid and dissolved in ferrite.

Methods to determine total carbon:

A. Direct treatment of material to produce CO₂ from C present.

1. Combustion in oxygen.
2. Combustion with CuO and KClO₃.
3. Combustion with CuO in oxygen.
4. Combustion with KHSO₄.
5. Solution and oxidation with H₂SO₄, CrO₃ and H₃PO₄.

B. Volatilize iron then oxidize C to CO₂.

1. Volatilize in current of chlorine.
2. Volatilize in current of hydrochloric acid.

C. Solution of iron and combustion or weighing of residue.

Solvents: Cupric-potassium chloride, cupric chloride, iodine, bromine, fused silver chloride, cupric sulphate, electrolysis in dilute hydrochloric acid.

The method using cupric-potassium chloride as solvent with subsequent combustion of the residue has long been regarded as the most accurate method. Its precision has been amply demonstrated. The method is somewhat tedious.

The method of direct combustion required very fine material and often gave low results by inclosing unburned metal when starting the combustion with a cold furnace; directions also called for heating at a good red heat 45 minutes after the furnace was hot.

According to our directions we start the combustion of an ordinary sample in a hot furnace, best between 1,000 and 1,100° C.; combustion is rapid and complete. This method is rapidly superseding all others for all classes of work.

Alundum (fused Al₂O₃) sand in an alundum boat holds the fused iron oxide best of any available material; silica or porcelain would fuse with the oxide to form an easily fusible slag where the alundum acts merely as an absorbent.

The absorption bulbs are always weighed completely filled with oxygen. Small glass plugs are provided to close the openings at the moment of disconnecting. Serious error results if the bulbs are weighed filled with air at one time and with oxygen at the other.

For the determination of graphite hydrochloric acid has sometimes been used as the solvent; results do not necessarily agree with the nitric acid method for car-

bon separated from cementite may also be included, giving high results. Always use acid of exactly the same strength and heat gently, only, when dissolving. 3/11 of the increase in weight of the bulbs is due to the carbon in the sample; chemical factor = .2727.

The Eggert method of determining combined carbon by the color given to its nitric acid solution was introduced in 1862. It is recognized as a comparison method only for material of similar origin and treatment.

Consult the treatise by Blair for a full exposition of the whole subject. H. B. PULSIFER.

Vanadium and Chromium in Steel.

Unless it is known that vanadium is present in the steel, it is best to test for it qualitatively. This may be done quickly by dissolving about .5 gram in dilute sulphuric acid (1:3) in a large test tube. Heat and add a little water if necessary to obtain complete solution. Add 5 cc. concentrated nitric acid and boil to disappearance of red fumes. A yellow precipitate at this point indicates tungsten and must be filtered off using dry paper without washing. Place 5 cc. of the solution, filtered or not as necessary, in each of two test tubes. To one add 5 cc. sodium peroxide solution (.35 gm. Na₂O₂ in 12.5 cc. of 1.3 sp. g. H₂SO₄ and diluted to 50 cc. with H₂O). To the other add 5 cc. water. Vanadium gives a brown color or brick red in large amounts with Na₂O₂, which may be detected even in the presence of considerable chromium by using a white background for comparison. In case titanium is suspected, the color is discharged slowly with dilute ferrous sulphate. Titanium shows a bright yellow while with vanadium only, the red or brown goes to colorless. The colors are more difficult to detect with chromium present.

If vanadium is known or found to be present, dissolve 4.0 grams steel in 60 cc. dilute sulphuric acid (1:4). Oxidize carefully with strong nitric acid avoiding great excess. Evaporate to fumes on a hot plate, cool, dilute with 150 cc. water and boil till dissolved. Add slight excess of 2.5 per cent solution of KMnO₄, boil about five minutes and add a little manganese sulphate if some permanganate is still undecomposed. Cool and dilute with water. The solution may be made to 500, filtered through a dry filter and 375 cc. used, or it may be filtered through asbestos, washed fifteen times with dilute sulphuric and the whole solution used. In either case add 50 cc. dilute sulphuric acid (1:4) and run in excess N/10 ferrous ammonium sulphate. If much chromium is present, the standard should be added till no further darkening takes place, then a few cc. in excess. Titrate back with N/10 KMnO₄ till just permanently pink. A little practice is necessary to catch the pink "glint" through the chrome green. If in doubt, add another cc. ferrous sulphate and come back slowly to the first trace of pink. The excess ferrous sulphate represents the chromium in the sample. 1 cc. N/10 ferrous sulphate represents .001743 gram Cr.

Add about 3 cc. N/10 or 6 cc. N/20 ferrous sulphate, making sure that an excess is present. Titrate back with N/20 potassium bichromate, using potassium ferricyanide as an external indicator. The complete disappearance of the blue is used as the end point but it is best to run a blank with a non-vanadium chrome steel. If an N/20 bichromate solution is not at hand, the solution from the chromium may be titrated directly with ferrous ammonium sulphate, using about .5 cc. ferricyanide as an *external* indicator. The first green coloration free from brown or the first darkening of the green solution depending on the amount of chromium present, is taken as the end point. As in the other case a blank is necessary. 1 cc. N/20 $K_2Cr_2O_7$ represents .00256 gram vanadium.

Tungsten in Steel.

To 2.0 grams of steel in a Jena beaker or casserole, add 50 cc. 1.16 HCl (5:1) and heat nearly to boiling. Add carefully, a few drops at a time, concentrated nitric acid, allowing the frothing to cease between each addition. If done, carefully, the steel may be decomposed without separation of tungstic acid and the time of operation greatly reduced. Boil to about one-third the bulk, add 80 cc. water, and boil. The precipitate should be a clear bright yellow. If not, digest till it "clears." The stirring rod should *not* be allowed to remain long in the presence of the tungstic acid as it is perceptibly dissolved. Filter and wash with hot and very dilute HCl till free from iron. The precipitate may be impossible to remove completely from the walls of the beaker. In this case, use a small piece of filter paper moistened with ammonia. Place it in the filter after washing is complete. Dry, filter and ignite at a very low temperature in a platinum crucible. Precipitate consists of SiO_2 , Fe_2O_3 and WO_3 and perhaps Cr_2O_3 . Add a drop or two sulphuric acid and a few cc. hydrofluoric acid. Ignite at a low red. The loss is SiO_2 . Fuse the residue completely with sodium carbonate (2 to 3 grams), allow to cool, add 50 cc. water and boil. When all that is soluble is in solution, filter and wash with hot water. Ignite the precipitate to Fe_2O_3 and subtract from the previous weight. The difference is WO_3 unless chromium has been in the precipitate. In this case the filtrate from the iron will be yellow and chromium must be determined. Since only chromium tungsten and possibly molybdenum are present, any rapid chromium method will answer the purpose. The chromium, if any, is subtracted from the weight after deducting the iron. The remainder is WO_3 in which the factor for tungsten is .7931.

Molybdenum in Steel.

The filtrate from the tungstic acid (see above) may be made to 500 cc. and one-half taken for silicon and phosphorous. In the tungstic acid there will be a small amount of molybdenum which should be taken out after the iron by reducing the filtrate with tartaric acid (2 grams), acidifying with sulphuric acid and passing in hydrogen sulphide. The brown sulphide of molybdenum is precipitated if the solution is very

faintly acid till saturated with sulphide, and the acidity then increased. Filter off the sulphide if any is formed, wash with very dilute acid containing hydrogen sulphide and ignited to oxide at a very *gentle* heat. MoO_3 times .6666 gives Mo. The tungsten must be recalculated if molybdenum is found.

The main part of the molybdenum is contained in the filtrate from the tungstic acid. Add NaOH solution to one-half the filtrate till neutral, but no permanent precipitate is produced, or darkening in color. Dissolve 7 grams caustic soda in 150 cc. water and heat nearly to boiling in a 500 cc. graduated flask. Run in the above neutralized solution in rapid drops, shaking the flask vigorously. Dilute to the mark, shake well and filter through a *moistened* 28 cm. filter in an 18 cm. funnel. Throw away the first of the filtrate, then collect 250 cc. in a graduated flask. Wash into a beaker, acidify with hydrochloric and add 4 cc. concentrated acid in excess. Add excess sulphurous acid, boil, add 40 cc. ammonium acetate (made from acetic acid and ammonia) and 6 cc. of lead acetate (10 gms. per liter acid with acetic acid). Filter off the lead molybdate, dry and ignite in porcelain. The precipitate is not volatile at high temperatures. $PbMoO_4$ times .2615 gives molybdenum.

Nickel in Steel.

Dissolve 1.0 gram steel in about 25 cc. 1.16 hydrochloric acid (5:1). Heat until in solution, adding a little more acid if necessary. If not completely soluble, filter and wash with hot water. Add about 1 gram tartaric acid and heat solution to about 50° C. Make a solution of dimethylglyoxime (2.5 gm. in 220 cc. of 98 per cent ethyl alcohol) and add sufficient to precipitate nickel. For 1 per cent nickel use 20 cc., 2 per cent use 40 cc. and so on. Add dilute ammonia till just neutral or very faintly alkaline, and the nickel is precipitated as a brilliant scarlet flocculent precipitate. Filter through paper or gooch and wash well with hot water. If paper is used, the precipitate must be washed into a weighed dish. The gooch or dish is dried at 100° C. and weighed. It consists of $C_8H_{14}N_4O_4Ni$, and contains 20.332 per cent nickel. *Note*—If this method is to be used for high nickel alloys, the precipitate is apt to contain some impurities due to the large bulk. In this case it may be redissolved in very dilute acid, before drying and reprecipitated with ammonia. The second filtrate should be tested with the reagent to be sure it is free from nickel. The precipitate may also be ignited to nickel oxide and by using the nickel factor .7858, the weight of nickel obtained and checked against the previous figure. Discrepancy usually means iron which may be determined by dissolving up the ignited oxides.

According to first estimates this year's average sugar beet crop in Belgium amounts to 14.73 short tons per acre, yielding 16.5 per cent of sugar. At present contract prices the farmer who was paid at the rate of \$4.90 per short ton on a 14 per cent sugar basis will receive \$5.95 per short ton.

METALLURGY

INDUSTRIAL APPLICATION OF MICROSCOPIC METALLOGRAPHY FOR CONTROLLING THE WORK PUT ON COPPER AND BRASSES.*

By CAPTAIN C. GRARD, PARIS.

The brasses forming the subject of this investigation are of best quality, very malleable in the cold, but fragile and short when hot.

By means of a careful determination of the cold working, accurate measurement of the annealing temperatures, and a very strict micrographical analysis constantly checked by mechanical tests, it was proposed to establish the various industrial products in question on a more scientific and therefore more certain basis.

METHODS OF TESTING EMPLOYED.

I. TENSILE TESTS.

Test bars. These had the following dimensions:

Brass 67/33—

Bars, 6 mm. thick, 10 mm. wide; 100 mm. long between grips.

Bars 0.3 mm. thick, 14 mm. wide; 100 mm. long between grips.

Brass 90/10—

Bars 2 mm. thick, 10 mm. wide; 100 mm. long between grips.

Copper—

Bars 2 mm. thick, 10 mm. wide; 100 mm. long between grips.

One of the heads of each bar was longer than the other, to enable a micrographic specimen to be detached after the preliminary treatment and before the tensile test.

Cold Working. When brought to their final dimensions, the bars exhibited a well defined effect of cold working, as will be explained further on. To produce this effect, recourse was had to successive cold rollings without any intermediate reheatings:

Annealing. This was carried out as follows:

1. Annealing below 650°: Between 200 and 650° the annealing was carried out in a bath consisting of equal parts of potassium nitrate and sodium nitrite, heated by gas.

The temperature was measured by means of a mercury thermometer up to 360°; but between this point and 650° it was ascertained within a margin of about 5° by means of a Siemens & Halske pyrometric galvanometer.

2. Annealing above 650°: These annealings were performed in a gas-fired muffle furnace, the temperature, in this case also, being measured with a Siemens & Halske galvanometer. Some annealings were also carried on in the furnace from 600°, so as to have temperatures in common with those of the first series and thus enable the two modes of annealing to be compared.

After passing through the various treatments (cold working, annealing, quenching), the bars were subjected to tensile tests, and the micrographical test piece was detached and examined.

Tensile Testers.—The large test pieces were tested in a 20,000-kilo vertical machine, standardized direct. The other machines were of 5,000, 1,000 and 500 kilos capacity, and either standardized direct or by means of dynamometers in comparison with directly standardized machines.

The elastic limit in particular formed the object of very accurate determinations, by means of a cathetometer apparatus mounted on the bench of a horizontal tensile tester.

By this means it was possible to measure with great precision:

1. The elastic limit.

2. The elastic elongation; that is to say, the data forming a basis for calculating the modulus of elasticity.

2. MICROGRAPHICAL TESTS.

The micrographical specimen forming part of the test bar was detached from the latter after the final treatment, and was marked with the same number as the corresponding bar.

Polishing was effected in accordance with the principles laid down by Mr. Le Chatelier, that is to say by means of very finely divided alumina held in suspension in water.

Etching.—For 67/33 brass, the following solution was employed:

Water	100 cc.
HCl	6 cc.
Ferric chloride	19 grms.

For 90/10 brass:

Water	100 cc.
HCl	50 cc.
Ferric chloride	5 grms.

The specimens were micrographically examined and photographed by the aid of the Le Chatelier microscope; and in this manner special attention was bestowed on 67/33 brass, or cartridge brass, 90/10 brass and copper.

1. 67/33 BRASS, OR CARTRIDGE BRASS.

As can be seen, in accordance with the Charpy diagram showing the variations in the breaking load and percentage elongation according to the proportion of zinc, the 67/33 alloy exhibits a combination of strength and malleability, since the maximum elongation corresponds to a zinc content of 30 per cent and the maximum strength to 45 per cent.

It is very closely allied to brasses of the second category, having a percentage of zinc which is very high for a brass of the first category. The cost price is

*Paper presented at the 6th Congress of the International Association for Testing Materials.

consequently lower than that of the other alloys of the first category that are suitable for use—alloys richer in copper.

The brass forming the subject of examination was one which satisfied the Specification imposed by the War Department for the supply of 67/33 brass, viz:

Margin allowed in composition ± 0.6 .

Impurities < 0.45 per cent, of which not more than one-half may consist of any one ingredient.

Mechanical properties: $30.6 \text{ kilos} < R < 34 \text{ kilos}$.

$A > 57\%$.

Without having in any case $15 R + 6 A < 812$.

Condition in Respect of Cold Working.—The completely annealed brass exhibits no effect of cold working. The definition of complete annealing will be given later.

The bars, having been cold worked by successive passes through a powerful rolling mill, were brought by cold working to the dimensions:

Width = 14 mm.

Thickness = 6 mm.

The effect of cold working was determined by the sectional variation per sq. millimetre.

S , being the original section of the bar, and

s , the final section

the cold-working value is represented by the following equation

$$\text{Cold working} = \frac{S - s}{s} \times 100,$$

which gives the value 100 when the final section becomes one half the original section.

This method of expression is of course an arbitrary one. The percentage effect of cold working, which is thus a function of the deformation, does not in the least impair the value of the mechanical properties, which value may remain stationary whilst the deformation, that is to say the percentage of cold working effect, may increase.

The bars exhibiting a definite cold working were machined to the following dimensions:

14 by 6 mm. for the heads,

10 by 6 mm. for the body of the bars.

They were then subjected to tensile and micrographical tests, after passing through the requisite heat treatment.

The same methods were employed for examining the thin brasses, the bars being brought down to a thickness of 0.3 by systematic rolling which enabled the cold working effect to be determined.

Variations in the Properties of Cartridge Brasses as a Function of different degrees of Cold Working.—An endeavor was made to ascertain the law relating to the variations in the mechanical and micrographical properties of 67/33 brass as a function of the different degrees of cold working. This law is represented by the diagram (Fig. 1), from which it can be seen that

a cold-working value of 40 per cent almost completely destroys the ductility of the brass.

The cold-working effect is calculated from the variation in section per

$$\frac{S - s}{s} \times 100$$

sq. mm.

a Charge au rupture = Breaking load.

b Allongements = Elongations.

c Limit élastique = Elastic limite.

Beyond a cold-working value of 200 per cent the action on the mechanical properties is inappreciable; but the risk is incurred of causing the alloy to deteriorate and crack.

Variations in the Micrographic Structure as the result of Cold Working.—In the fully annealed condition the alloy presents highly characteristic octahedral crystals. These crystals are broken down by cold working. When the cold working effect is produced by rolling, the direction of rolling begins to be made apparent by the direction of elongation of the crystals,

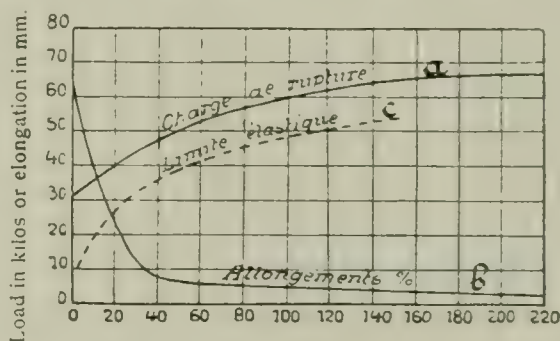


Fig. 1.

when the cold-working value attains about 40 per cent.

The crystals then flatten, and beyond 150 per cent are transformed into long, tenuous striae. Finally, these lines end by resolving themselves into white dots when the cold working is very energetic and incompatible with the preservation of the alloy.

Variation in the Mechanical Properties and Micrographic Appearance of Cartridge Brass, as a function of the Annealing Temperature.—The cold working value of the bars was 125 per cent.

The annealing was performed under the conditions indicated, two bars being treated at each temperature.

Between 100 and 400° the temperatures at which the bars were heated differed by 10° between one experiment and the next. From 400 to 800° the interval between the temperatures was 25°; and from 800 to 920° the interval was 25°.

The bars were kept in the heating furnace for 30 minutes.

Variation Produced in the Mechanical Properties by Annealing.—The diagram, Fig. 2, illustrates the "Law" of the variations produced in cartridge brass by the annealing temperature. Examination of this diagram reveals the existence of five zones:

1. Zone from 0 to 250° (approximate), or zone of complete cold working. In this zone the elongation is very slight, whilst the strength is double that of the annealed brass. In this zone the influence of the temperature is nil.

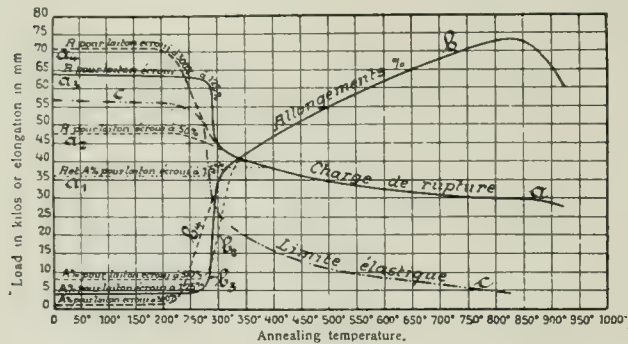


Fig. 2.

a Charge de rupture = Breaking load.

b Allongements = Elongations.

c Limite élastique = Elastic Limit.

a₁ Rel. A% pour laiton écroui à 15% = For brass cold worked to 15%.

a₂ R. pour laiton écroui à 50% = For brass cold worked to 50%.

a₃ R. pour laiton écroui à 125% = For brass cold worked to 125%.

a₄ R. pour laiton écroui à 300% = For brass cold worked to 300%.

b₂ A % pour laiton écroui à 50% = A % For brass cold worked to 50%.

b₃ A % pour laiton écroui à 125% = A % For brass cold worked to 125%.

b₄ A % pour laiton écroui à 300% = A % For brass cold worked to 300%.

2. Zone between 250 and 350°, or relaxed zone. The properties change in a very sudden manner, and the brass is, as it were, in a relaxed state.

3. Zone between 350 and 750° (approximate). This is the zone in which the properties modify slowly, and in which the brass which was relaxed in the preceding zone, passes over into the fully annealed condition as defined later on.

4. Zone between 750 and 850° (approximate), or zone of complete annealing. This is the zone in which the degree of annealing remains constant, that is to say in which the properties of the alloy are appreciably the same whatever the temperature at which it is annealed within the limits of this zone.

5. Zone between 830° and fusing point. In this zone, both the breaking strength and elongation diminish, and the elastic limit falls nearly to zero. This is a bending zone.

Modulus of Elasticity.—The mean value for the modulus of elasticity is: 8,000.

Variations Produced in the Metallographic Structure by Annealing:

1. Zone of complete cold working. The octahedral crystals are broken, flattened and pressed.

2. Relaxed zone. This zone is characterized, from the micrographical standpoint, by the disposition of the deformed crystals and by the appearance of perfectly grouped, very small crystals lying closely packed together.

3. Recupération zone. The crystals gradually increase and their contours become progressively improved in definition.

4. Zone of complete annealing. The crystals have attained their maximum dimensions.

5. Bending zone. This is frequently characterized by the appearance of small bubbles of gas, the alloy then gradually approximating to the crude, cast alloy.

Practical Conclusions.—The first two zones should never correspond to a finished condition of the worked metal. In the zones wherein the crystals exhibit a compressed and deformed appearance, the brass is not in a state of stable equilibrium.

Zones 3 and 4 alone correspond to a finished condition; and the place of the alloy in the 3d zone depends on the mechanical properties desired. In zone 4, in view of the probable presence of impurities, it is not advisable to exceed an annealing temperature of 760°.

Zone 5 should be avoided. Furthermore, the experiments show that it is economical and without danger to the metal to associate a high annealing heat with extensive cold working.

Extending the Investigation.—The foregoing investigation has been extended by starting with different degrees of cold working in place of 125 per cent only.

Beyond the relaxed zone the diagram gives identical annealing results. With increased cold working the relaxing takes place earlier, and vice versa (see Fig. 2).

Dynamic Cold Working.—Dynamic cold working produced by the aid of a drop hammer gives the same results as that obtained statically.

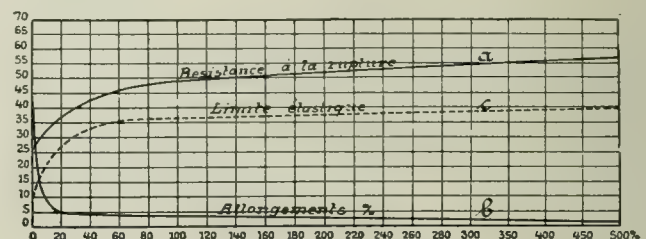


Fig. 3.

Bars 0.3 mm. Thick.—The annealing experiments with cold-worked bars 0.3 mm. thick, gave the same zones, with bending above 650°.

Influence of the Duration and Temperature of Annealing.—The study of the influence of the time (t) and temperature (T) of annealing — f (t, T) — has furnished highly interesting results, enabling one to manipulate the factors T and t so as to obtain any desired properties (hardness, elastic limit, etc.).

In this way one can obtain, as a function of the time and temperature, a curve representing the geometrical situation of the points corresponding to the annealings which are able to impart the desired properties to the brass, with relation to the geometrical situation of the points of equal micrographic structure. Similar curves

have rendered considerable service in connection with the manufacture of brass cases.

Micrography thus constitutes a valuable and often unique means for ascertaining whether the desired final condition has been attained, and especially whether the annealing has been sufficient to cause the brass to pass out of the zone of complete cold working or of the relaxed zone, that is to say whether annealing has brought the brass into a condition which will ensure its durability.

II. 90/10 BRASS.

The examination of 90/10 brass was carried on under the same conditions as that of cartridge brass. It was less extensive than the previous investigation, because advantage was taken of the explanations furnished, the methods set forth and the result detailed in connection with cartridge brass.

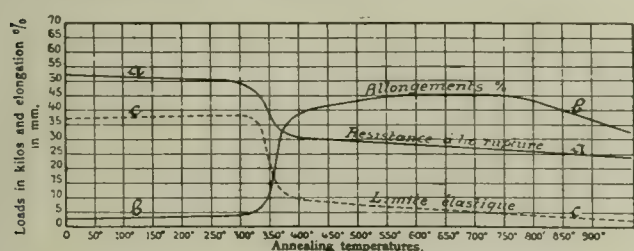


Fig. 4.

The brass employed was in the form of wire, 7.32 mm. in diameter, and satisfying the following mechanical conditions:

$$R > 25 . A > 42.$$

Variations produced in the mechanical and micrographical properties of 90/10 brass by different degrees of Cold Working.—The results of the mechanical tests are summarized in the following diagram (Fig. 3). Moreover, the indications furnished by the micrographical examination are perfectly concordant with those yielded by the mechanical tests.

Variations produced in the mechanical and micrographical properties of 90/10 brass, as a function of the annealing temperature.—The five zones already mentioned in connection with the annealing of cartridge brass, were also observed in this material (see diagram, Fig. 4).

III. COPPER.

In order to obtain the purest possible material, the copper selected for this investigation was electrolytic copper, that is to say a material containing not more than 2.5 per cent of foreign substances and 1.5 per cent of oxygen.

It satisfied the following mechanical conditions:

$$R > 22 K . A \% > 40.$$

Variations produced in the mechanical properties and micrographic structure of electrolytic copper by different degrees of Cold Working.—See accompanying diagram (Fig. 5).

For cold working from 100 per cent onward, no further working has any influence on the strength, elastic limit or elongation of the metal.

From the micrographical point of view, the crystals forming in the zone of complete annealing are considerably smaller in the case of copper than those in 90/10 brass in the same zone.

These crystals flatten quickly under a relatively slight cold working, and a large number are almost filiform when the cold working does not exceed 50 per cent.

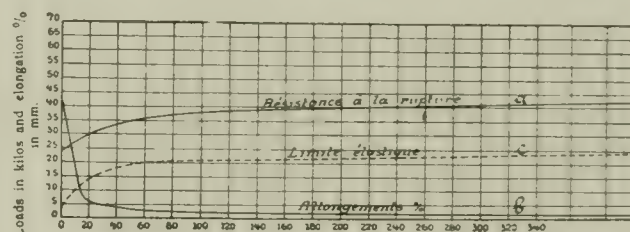


Fig. 5.

Variations produced in the mechanical and micrographical properties of copper by annealing at different temperatures.—Examination of the accompanying diagram (Fig. 6) reveals the zones already mentioned.

The zone of cold working is very narrow, the range being only about half that of 90/10 brass. Complete annealing is already attained at 400°.

From the micrographical point of view, the striae produced by cold working are very well defined up to 150° that is to say during the zone of complete cold working. They gradually disappear in the relaxed zone.

In the zone of recuperation, the crystals are formed, but are far smaller in dimensions than in the corresponding zone and a fortiori than in that of 90/10 brass.

The crystals formed in the annealing zone are equal

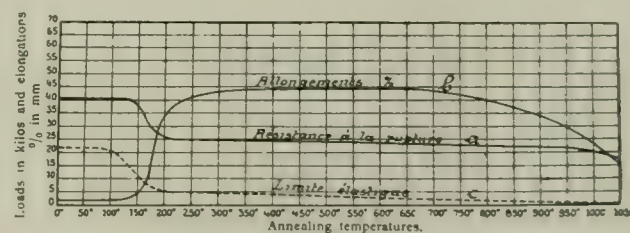


Fig. 6.

in dimensions to those formed in 67/33 brass when annealed at 500°, and those in 90/10 brass when annealed at 600°.

IV. CONCLUSIONS.

Copper, 90/10 brass and 67/33 brass are very sensitive to cold working, a relatively small amount of work—well defined in each case—being sufficient to deprive them of their malleability.

Examination of the process of annealing after cold working has revealed 5 well defined zones, of which Nos. 3 and 4 alone correspond to a final condition. The principle of recuperation after cold working is established.

The foregoing investigations have demonstrated the valuable aid furnished by micrographical examination as a check on industrial practice.

The microscope reveals the molecular condition of the alloy in a very decided manner. After showing the brass damaged by cold working, the microscope shows it regaining its equilibrium on issuing from the relaxed zone; then exhibiting extremely fine crystals on entering the zone of recuperation, which crystals go on increasing progressively in size up to the zone of complete annealing.

Each micrographical structure is associated with definite mechanical properties and malleability.

These principles have been applied in manufacturing practice; and in this way, by comparison with micrographical specimens forming a kind of photographic scale, one is able to recognize:

1. The mean value of the cold working to which the manufactured material has been subjected.
2. Which portion of the material has been worked the most.
3. The necessary modifications to be introduced into the manufacturing process in order to obtain a better distribution of the work.
4. The additional work which can, if necessary, be put on the metal, for a given molecular condition of the material. This has often enabled annealings to be dispensed with, thereby effecting a saving in the cost of manufacture.

After annealing following cold working it is possible, by the aid of specimens systematically prepared in accordance with a micrographic scale, to determine the annealing or recuperation value in all cases.

In the case of recuperation more particularly, it can be ascertained whether the material is really in such a final condition as will ensure its durability. This application is one of the most important of all.

In the manufacture of brass articles it may be desirable not to subject the whole or a portion of same to complete annealing which might render the material too soft and easily deformed.

It is, however, necessary to ascertain, by the aid of micrography, that the process of recuperation has brought the brass out of the relaxed zone and cold-worked zone, which do not accord with a state of equilibrium of the alloy and will give rise to fissures and cracks. This micrographic check has enabled serious defects to be obviated which had previously been the cause of the loss of a considerable number of articles.

5. It is also possible, by micrographical examination, to ascertain whether the brass has not been brought into the bending zone as the result of annealing at too high a temperature.

In short, empirical processes must give way completely to scientific methods, which latter alone are capable of ensuring valuable and constant results. This is the most important conclusion arising from the present study.

TYPICAL AMERICAN USES OF CAST-IRON, AND TEST METHODS APPLICABLE TO THEM.*

By JOHN JERMAIN PORTER, STAUNTON, VA.

American foundry practice has made great progress in passing from the empirical stage to that of scientific control. A most important feature, the use of chemical analysis as a basis for mixing irons, is now practically universally adopted, but much still remains to be done both in the more efficient use of chemistry and in the adoption of other scientific methods of control.

It is now becoming quite widely recognized that chemical composition is not the only factor determining the properties of cast-iron, but, although the importance of structure is known, the methods of metallography have received very little attention from foundries and users of castings. It is true that investigators have used the microscope on cast-iron with valuable results, but this method of control has not yet been generally taken up in practice, as in the case of steel. The two reasons which apparently account for this neglect are: first, the fact that foundries, being operated in smaller units, have as a rule less technical skill available at each individual plant; and, second, that the more complex structure of cast-iron makes the interpretation of its microstructure much more difficult. It is probable that much of the metallurgical progress of the near future will be along this line.

The theory that oxygen and nitrogen may be present in cast-iron and are accountable for some otherwise inexplicable phenomena is gaining ground among practical foundrymen, and means of eliminating these elements are being widely adopted. Greater care is being given the cupola process, and the use of ferromanganese, silicon, vanadium and titanium as deoxidizers is rapidly increasing. Ferro-alloys are also rather extensively used to correct the composition of the iron in the ladle.

Since cast-iron is used for a wide variety of purposes, it is obvious that the properties by which its value is measured and the tests to which it is subjected should be different for each class of castings. Hence it is necessary to consider each class separately. It is true that current practice does not, as a rule, adequately recognize this fact, and almost the only test which is commonly applied is that for transverse or tensile strength, although this property in many or perhaps the majority of cases is not of chief importance. There are but few foundries in this country devoting attention to getting special properties in this material, and to most foundrymen, as well as users, cast-iron is simply cast-iron, and a casting is satisfactory when true to pattern and free from visible defects.

*Paper presented at the Sixth Congress, International Association for Testing Materials.

The succeeding portion of this paper will discuss some characteristic American uses of cast-iron, the properties needed, recent progress in meeting these needs, and the tests necessary to define the desired properties.

MACHINERY CASTINGS.

A large percentage of machine parts are made of cast-iron, which material is especially adapted for this use on account of the ease with which it is cast and machined into the desired shape. The more important properties desired in machinery castings are softness, strength, and a fine grain-structure, in addition of course to freedom from visible defects, such, as blowholes, cracks, shrinkage cavities, etc.

It is an easy matter to make soft castings, but to get the combination of easy machining properties, strength and close grain, as demanded by some users, has proved a difficult proposition to many foundries. Especially is this true as to closeness of grain and the ability to take a high polish, which is so desirable on many finished parts. The solution has been reached in various ways. The use of charcoal iron is one method, satisfactory except from the standpoint of cost. Certain brands of coke irons are found to give greater strength and closer grain for a given softness than others, and the knowledge of such mixtures is a valuable asset to the practical founder. Another method is found in the use of steel scrap in the cupola mixture, making the so-called semi-steel, which gives a closer grain-structure and considerably more strength without material change in composition. The treatment of the metal with certain ferro-alloys has also been found advantageous in this connection.

The buying of machinery castings would be greatly simplified if definite limits of hardness, strength and grain size could be specified. Satisfactory methods for testing hardness are found in the drill test and the Shore scleroscope, most of the various other proposed methods being too cumbersome for commercial use. The drill test, simulating as it does actual machining operations, gives the more reliable results, while the scleroscope possesses the advantage that it can be used directly on the casting without in any way injuring it.

For testing the strength of cast-iron there are available the ordinary transverse, tensile and compressive tests, the first of which is, in the opinion of the writer, preferable. In the testing of strength (and hardness also), it must be remembered that the properties of cast-iron depend in part upon the thickness of the section, and hence that, in cases where it is not possible to test the casting itself, the testpiece should at least approximate the section of the casting. Probably three standard sizes of test-bars could be selected, to represent the three classes of light, medium and heavy castings. The broken ends of these bars could be then used for the drill test to determine hardness.

For grain size there is no practical test available; a serious lack, as in many cases this property is of

the greatest importance. Possibly something might be done with a planimeter used on a microphotograph of standard magnification; a rough test, of value in some cases, can be made by comparing the fracture of a broken test-bar with a scale made of previously broken test-bars of varying grain size.

The freedom from blowholes and other casting defects is best determined by ocular inspection. Unfortunately, there is no method of inspecting the interior of the casting without destroying it, and while the tendency of the iron to shrinkage, blowholes, etc., can easily be tested, such tests would be of doubtful utility, since these troubles are frequently, if not usually, due to faulty molding and pouring.

HYDRAULIC WORK.

Cast-iron is still very generally used for this class of work, on account of the ease with which it is formed into shape, although there has been some attempt to substitute steel for very high pressures. The properties desired in the metal are practically the same as in the preceding case, except that they stand in a different order of importance, close grain and freedom from shrink-holes and spongy places being the first consideration. Much the same means are used to obtain the combination of density strength and the ability to machine easily, but as the importance of density is greater in this case, the use of special means, such as charcoal irons, steel scrap and ferro-alloys, is more frequent.

The most direct and satisfactory test for hydraulic work is to subject the casting itself to some specified hydraulic pressure. In many cases, however, the casting cannot be so tested until a good deal of expensive machine work has been done on it, and in this event it seems advisable to specify the strength and hardness tests previously described. The hardness test should be used in any case, as the bursting strength does not, of course, give any idea as to machining properties. A test for grain-structure would be especially valuable in connection with this class of work.

ELECTRICAL MACHINERY.

For parts where high electrical permeability is of prime importance, cast iron has been largely displaced by steel, but in the majority of cases it still holds its own on account of the greater ease of forming. The permeability of cast iron, although always low as compared with that of the purer forms of iron, can be considerably improved by keeping the manganese very low and the silicon quite high. In practice, however, not much attention is usually given to this property, since the greater number of castings are used in parts of machines not carrying the magnetic lines of force, and hence having requirements not different from ordinary machinery castings.

In electrical castings a permeability test used in conjunction with strength and hardness tests should be sufficient to define the quality of the material. Since permeability probably bears a fairly close relation to

chemical composition it might be possible, although certainly less satisfactory, to specify analysis in place of permeability direct.

HEAT-RESISTANT AND CHEMICAL-RESISTANT CASTINGS.

A large variety of castings come under this head; the best known examples are probably ingot molds and grate bars. Only a few foundries are giving attention to producing castings of these special properties, and there is but little generally available information. Grate bars, for example, are ordinarily made of the cheapest possible mixture irrespective of its quality as regards service. In the case of ingot molds, on the other hand, some pains are taken to obtain the special quality of heat-resistance, and a low-phosphorus iron is always used for this purpose.

There are no tests for heat-resistance and chemical-resistance of cast iron in common use. For heat-resistance it is a very difficult matter to devise any single test which will answer for all classes of castings, since the effects of heat are manifested in several different ways. Chemical analysis may be specified with advantage in some cases, since the melting-point of cast iron depends chiefly on this factor. Resistance to the action of chemicals can be tested directly without much difficulty in a manner similar to the accelerated corrosion test used on steel. There is, however, great need for the standardization of all conditions under which such tests are made, so that comparable results may be obtained.

CHILLED CAST IRON CAR WHEELS.

These form one of the most interesting applications of cast iron in American practice. The service conditions for these wheels are very severe. The load on each wheel often amounts to between 10,000 and 20,000 lbs. They are constantly subjected to heavy blows due to pounding at rail joints. The friction of the brakeshoes induces severe heat strains in the tread. Finally the users of these wheels demand that they have a high resistance to wear. Owing to the nature of their service any failure is apt to be attended with very serious results, and hence great pains must be taken to insure a uniformly high quality of product.

The results desired are produced by the use of both special materials and special methods of casting. Formerly charcoal iron was used exclusively for this class of work, but now coke iron enters largely into the mixture. The problem of a high-grade mixture has been much complicated by the necessity of remelting the old wheels, with their usual high content of sulphur. A partial corrective for the excessive amount of scrap which it is often necessary to use is found in the addition of ferromanganese, and there have also been obtained some encouraging results through the use of ferro-titanium.

The special methods of casting consist in the use of a circular chill in that part of the mold forming the tread of the wheel. This method has been frequently described and needs no discussion. With the proper percentage of silicon this results in the tread being

chilled to a depth of about $\frac{3}{4}$ in., back of which is tough gray iron. The chilled tread is, of course, intensely hard and exceedingly resistant to wear, while the wheel as a whole is very tough and has proven eminently satisfactory in service. Steel wheels, long used on passenger cars, have recently been substituted on freight cars of very high capacity. They are, however, much more expensive and in some cases have not proven entirely satisfactory as to wear, so that there is every indication that the cast iron car wheel will hold its own for a long time to come.

The specifications and tests required for car wheels have been so often published and are so readily accessible that they need not be repeated at length. Briefly summarized the tests are carried out on a certain number of the castings themselves, and consist chiefly of a drop test to measure the resistance to shock and blows, a heat test made by pouring molten iron around the tread of the wheel, to measure the resistance to heat strains, and measurements to verify dimensions. It would appear that a hardness test on the chill might advantageously be added, in view of the known variation in the hardness of chilled iron. A test for wearing quality would be better still, but no satisfactory test of this sort is in sight.

CHILLED ROLLS FOR ROLLING MILLS.

Cast iron rolls still hold their own in sheet mill and some other classes of finishing work, although cast iron has been quite generally displaced by steel for the heavier service. In this case the service conditions are not unlike those to which car wheels are subjected, but they are even more severe as to heat strains. Moreover, owing to the great thickness of the castings the initial shrinkage strains are very great. The use of the very best grades of charcoal iron, together with air-furnace melting, is generally recognized as necessary for the successful manufacture of chilled rolls, chiefly on account of the difficulty with cracking due to heat strains. It is reported that the use of vanadium in chilled rolls is adding considerably to their wearing qualities.

For this class of castings there are no satisfactory tests in sight. It is inconceivable that any tests could be of value which are not made on the roll itself, and, while a difficult proposition it is possible that in time a set of tests similar to those used on car wheels may be devised.

BRAKESHOES.

Brakeshoes may serve as an example of the many smaller specialties which are made of cast iron. The requirements here are long life, with this limitation; that the hardness of the brakeshoe must be less than that of the wheel so that the wear will not be on the wheel. A close grain-structure is advisable, and in some cases at least is being obtained by the use of steel scrap in the cupola mixture.

For brakeshoes a wearing test used in connection with hardness limits would best define their quality. No satisfactory method of testing resistance to wear is in

sight, but it would seem that specifications for hardness alone could be advantageously used pending the development of such a test.

CAST IRON PIPE.

In point of tonnage, pipes are probably the most important castings made in this country. Cast iron is a particularly suitable material for pipes which are to be placed underground, on account of its relative resistance to corrosion as compared with steel and other commercially available materials. Competition is keen in this line, so that low-priced iron is necessary. Within the limitations set by price, close grain and strength are desirable, while hardness must be kept within such limits as will permit of a small amount of machine work.

In regard to the properties of the metal, none of the present specifications for cast iron pipe lay stress on anything other than strength as determined on a separately cast test-bar. A test for bursting strength and freedom from leakage made directly on the pipe would, of course, be a more accurate index of utility, but is probably too cumbersome for practical use. The transverse strength determination is probably as satisfactory as any simple test could be, but might with advantage be supplemented by specifying hardness limits.

STOVES AND FURNACE WORK.

Malleable cast iron and steel have been tried for stoves, but while they have perhaps a place, gray cast iron has proved more satisfactory and has steadfastly held its own. The service requirements here are resistance to the action of heat, resistance to warping, and a certain degree of strength. However, as these castings are very thin and are frequently highly ornamented, a very fluid iron is essential, and in practice the service requirements are deliberately ignored to facilitate manufacture. Resistance to heat requires low phosphorus, and resistance to permanent expansion, which causes warping, demands low silicon, but both phosphorus and silicon are invariably carried high in this class of work, to increase fluidity and make it easier to produce perfect castings. However, the product of our stove foundries is fairly satisfactory in service, and in appearance and finish has reached a high degree of perfection.

Specifications for stove and furnace castings should include tests for strength, hardness (since many parts have to be drilled), and resistance to heat. There is no trouble in regard to the first two tests, but, as previously stated, no good method has yet been devised for gaging heat-resistant qualities. Specification of chemical analysis can be used with advantage, but cannot be regarded as a really satisfactory substitute for the much-needed direct test for heat-resistance.

There are of course innumerable other uses of cast iron which might be described, but to make the catalogue complete would be an interminable task. In conclusion the fact should be emphasized that in many cases it is not possible to do much in the way of formulating specifications on account of the lack of suitable

methods of testing the properties. The apparent inclination of many users of castings to entirely ignore the quality of their material may be largely attributed to the lack of any definite numerical means of gaging quality.

POTASH EXPLORATION IN NEVADA.

The results of explorations for salines in Silver Peak Marsh, Nevada, recently made by the United States Geological Survey, are just published in a short report by R. B. Dole, of the Survey, as Bulletin 530-R, an advance chapter from Bulletin 530. Silver Peak Marsh is a salt playa or dried-up lake, of prehistoric origin, about 20 miles west of Goldfield and 25 miles southwest of Tonopah, two well-known mining centers of Nevada. The exploration was made for the purpose of ascertaining whether deposits of potash salts in commercial quantities lie within easy reach of the surface. No extensive beds of such salts were discovered, although the salts in certain samples of brine contain as much as 3.43 and 3.80 per cent. of potash (K_2O). Drill holes were sunk at several points in the old lake bed by means of a small, portable drilling outfit, operated by a burro, the borings being carried to a depth of about 50 ft.

Practically the entire surface of the playa, 32 square miles, is covered with salt that averages in depth about one-quarter of an inch. The upper muds, averaging probably 10 ft. thick, contain not less than 2 per cent. of salt. It is estimated that not less than 15 square miles of the northeastern part contains a 10-ft. saline bed, of which at least 60 per cent. is salt. It is calculated from these moderate estimates that 15,000,000 tons of salt lies within 40 ft. of the surface. The high rate of evaporation, which would permit solar concentration of brines, the absence of long-continued rainfall to interfere with operations, the nearness of a railroad, and more especially the high degree of purity of the product as indicated by analyses of the brines are extremely favorable features in regard to the possibility of utilizing these deposits.

Salt is now being produced on a small scale by Frank Porter, of Silver Peak, who states that about 150 tons have been bagged and sold in three years.

Some interesting data on the temperature of concrete during setting are given by Mr. W. D. Maxwell in a paper read before the Iowa Engineering Society. Tests were made during work on Des Moines river concrete bridge. The observations were made in various parts of piers and abutments composed of 1:3:6 concrete, with thermometers placed in pipes set in concrete. The points where readings were taken were from 3 to 10 ft. from surface and face of concrete. The temperatures recorded show an increase of 15° to 20° F. above temperature at time of pouring, in the concrete mass during setting, the maximum being reached in 7 to 10 days after pouring. Then the temperature falls, the rate depending on outside temperature.

PHENOL-FORMALDEHYDE CONDENSATION PRODUCTS.*

By L. H. BAEKELAND.

The resinous or amorphous products resulting from the action of phenolic bodies upon formaldehyde have lately attracted considerable attention on account of their rapidly increasing applications for industrial purposes.¹

It is questionable whether this general designation of "condensation products of phenols and formaldehyde" should be maintained much longer. Indeed, it is well known that these products can be obtained without the use of so-called formaldehyde. In fact, the first condensation products thus described were produced without the use of formaldehyde,² and it is generally accepted that other methylene compounds, for instance, methylal, trioxymethylen, hexamethylenetetramin, etc., can replace formaldehyde in this reaction. The fact that hexamethylenetetramin can suitably replace formaldehyde in the formation of the infusible phenolic condensation products was published as far back as Dec. 31, 1907, by Lebach.³

Lately, I have succeeded in producing fusible resinous condensation products identical with those described by Blumer, DeLaire, etc.,⁴ by introducing a mixture of salicylic acid and an inorganic acid in the cathode compartment of an electrolytic cell in which sodium chloride is electrolyzed, a mercury cathode being used. According to the well known reaction of Kolbe, the carboxyl group of salicylic acid is introduced by reacting with CO₂ on phenolate of sodium, so that we have here an example of the possibility of introducing indirectly the methylene group as CO₂, then reducing the carboxyl group by means of nascent hydrogen. A similar observation has already been recorded by Velden,⁵ who expected to get oxybenzylalcohol by reducing salicylic acid but obtained the corresponding saliretin-body resulting from the dehydration of phenol alcohol.

However, the designation "phenol-formaldehyde condensation products" has been so generally used that for a while, at least, we shall have to submit to it as a matter of routine.

In the same way we are erroneously designating as "formaldehyde" a commercial aqueous solution containing some real formaldehyde or methylen-oxide, CH₂O with much methylen-glycol, methylal, trioxymethylen, hydrates of trioxymethylen, other polyoxymethylen, etc., all compounds of methylen of which the technical value is equivalent in this reaction to that of true formaldehyde.⁶

The direct relationship of the resinous condensation products to phenol alcohols or their anhydrides seems now pretty well established. The so-called fusible soluble resinous condensation products are merely varieties of the saliretins,⁷ and all these products differ from each other only by greater or lesser fusibility, solubility or hardness, and each of these properties can be modified at will. Furthermore, we have the means at hand of producing all these bodies directly from phenol alcohols.⁸

The formation of ortho- and para-oxybenzyl-alcohol, or their homologs, by Manasse and Lederer, is sufficiently well known;⁹ this process consists in the direct action of one molecule of phenol on one molecule of formaldehyde in presence of one molecule of NaOH under special conditions:

Then DeLaire¹⁰ showed that these same phenol-alcohols can be transformed industrially, by dehydration, into fusible resins or saliretin products suitable for commercial purposes in place of shellac, copal or other natural resins. In that process, it is not necessary to first produce the phenol alcohol in pure form, and the two reactions can be carried out practically at the same time, so that the phenol alcohol is dehydrated to saliretin resins as soon as it forms.

This is accomplished more directly by reacting with phenol on formaldehyde in presence of an acid,¹¹ provided the reaction be carried out under suitable conditions. One of the required conditions is that the phenol should be in excess so as to avoid the formation of variable amounts of infusible and insoluble products. A fusible soluble saliretin can thus easily be prepared which has all the appearances of a resin; it melts if heated and solidifies by cooling; it is soluble in alcohol and acetone; it can be maintained in fusible condition for very long periods without becoming infusible or insoluble, provided heating be carried on below certain temperatures and provided the excess of phenol be not removed. This fusible resin and its preparation has been described by Blumer and DeLaire as a "shellac substitute," or "resin substitute,"¹² by Baekeland, who calls it "Novolak,"¹³ and lately again by Aylsworth, who calls it "phenol resin."¹⁴ In whatever way it be obtained, whether by using a phenol alcohol (DeLaire, Baekeland), whether by starting from phenol and formaldehyde in the presence of oxy-acids (Blumer) or in the presence of mineral acids (DeLaire, Thurlow, Bayer) or by the action of phenol on

*Raikov, Chem. Ztg., 26, 135; 12, 11 (1901). Kekule, Ber., 25, 2435. Harries, Ber., 34, 635; Compt. rend., 124, 1454; Bull. soc. chim., 17, 849. F. Auerbach, also Auerbach and Barschall, Arb. kais. Gesundh. Band, 22, Heft 3 and Band 27, Heft 1. Verlag Julius Springer, Berlin.

²Beilstein, Organ. Chemie, 2, 1109 (1896). R. Piria, Ann. Chem., 48, 75; 56, 37; 81, 245; 96, 357. Moitessier, Jahresbericht, 1886, 676. K. Kraut, Ann. Chem., 156, 123. Gerhardt, Ann. Chem. Phys., [3] 7, 215. F. Beilstein and F. Seelheim, Ann. Chem., 117, 83. C. Schotten, Ber., 1878, 784.

³Baekeland, Journal of Industrial and Engineering Chemistry, 1, No. 8, 545 (1909).

⁴J. prakt. Chem., [2] 50, 224. Ber., 1894, 2409-2411. D. R. P. Bayer, 85,588; U. S. P. Manasse, 526,786, 1894.

⁵DeLaire, British Patent 15,517, 1905; D. R. P. 189,262.

⁶Blumer, British Pat. 6,823, 1903; 12,880, 1902. DeLaire, French Patent 361,539. Wetter (Knoll), British Patent, 28,009; 1907. Knoll, French Patent 395,657; Bayer, D. R. P. 237,786; D. R. P. 201,261; British Patent, 26,317, 1907, etc.

⁷Loc. cit.

⁸Journal of Industrial and Engineering Chemistry, 1909, 545.

⁹U. S. Patent 1,029,737.

*Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

¹Baekeland, Journal of Industrial and Engineering Chemistry, 1, No. 3, 149 (1909); No. 8, 345 (1909); 3, No. 12, 932 (1911).

²Ber., 5, 1905; 19, 2009, 3004; 25, 3477; 27, 2411.

³Knoll patent, Belgium, No. 204,811, December 31, 1907. Ditto, Wetter (Knoll) British patent, No. 28,009, 1907, owned by the Bakelite Gesellschaft of Berlin.

⁴Baekeland, Journal of Industrial and Engineering Chemistry, 1, 545 (1909).

⁵Velden, J. prakt. Chemie, [2] 15, 164; Jahresbericht, 1877, 337.

formaldehyde without adding condensing agents (Story)¹⁵ or (Aylsworth) the product is absolutely the same in its chemical and physical properties. Its melting point or fusibility may be modified at will by varying the amount of free phenolic body. This free phenol exists in solid solution in the mass and can be eliminated by merely physical methods; by the partial elimination of this free phenol, the fusibility and the solubility of the resin are decreased. The last traces of free phenol cling tenaciously to these saliretin resins; so much, indeed, that at one time I was inclined to believe that this small amount of phenol was chemically combined. Indeed, the last traces of phenol cannot be expelled by heating at the lower melting temperatures of the product. There is nothing strange in this, if we take into consideration that phenol itself has a relatively high boiling point, and we know of numerous examples where colloids retain, physically, small amounts of other bodies which form therewith colloidal solid solutions. As long as there is some excess of phenol present in the saliretin, it is possible to maintain the mass in fusion for a practically indefinite time, provided the temperature be not raised too high. Pure saliretin, containing no excess of phenol, may be kept in fusion for some time, but after a while it polymerizes and becomes less fusible until finally it changes into some infusible product. However, it should be noted right here that this latter product, although it is infusible, does not possess the maximum mechanical strength nor hardness, nor general chemical and physical resistivity of those other polymerized infusible products, of which I will speak later on, and which are obtained by reacting with a sufficiently larger amount of formaldehyde, or equivalent methylen compounds, and which have been designated as Bakelite C.

It is possible to expel the slight excess of phenol which lends special fusibility to the so-called fusible resins; this can be accomplished whether these resins be called "shellac substitutes," "Novolak" or "phenol resins," or whether they be made directly from phenol alcohols or from phenol and formaldehyde with or without acid condensing agents. Indeed, plain heating at 300° C. to 350° C. or better, heating *in vacuo*, or in a current of an inert gas, like nitrogen, easily expels the free phenol and produces infusibility. The same result is readily obtained by entraining the free phenol by blowing superheated steam through the molten resinous mass.

These facts are corroborating proofs to others which establish clearly the saliretin-nature of these fusible products, and demonstrate their relationship to the phenol alcohols from which they are derived. If these fusible resins are prepared directly from phenol and formaldehyde, the preliminary formation of phenol alcohol may escape our notice, because by the action of heat on the mixture, especially in presence of acid bodies, the phenol alcohols are rapidly de-

hydrated to saliretin products. But it is quite possible to demonstrate their presence, and my assistant, Dr. A. H. Gotthelf, while preparing fusible resinous condensation products, by boiling a mixture of phenol and formaldehyde, acidulated by means of HCl, has been able to extract from this mixture well defined crystals of oxybenzyl-alcohol before the heat had accomplished its resinifying action.

It is self-evident that as soon as high temperatures are applied to such mixtures, the formed phenol alcohol will quickly undergo resinification, because the phenol alcohol will be dehydrated to a saliretin product as soon as it is formed.

If there is an excess of phenol present, or if the formaldehyde reacts in insufficient proportions, which amounts to the same thing, a fusible saliretin will be the result.

In the absence of an excess of phenol, but using however, a restricted amount of formaldehyde or other methylen compound, a polymerized infusible saliretin will be produced.

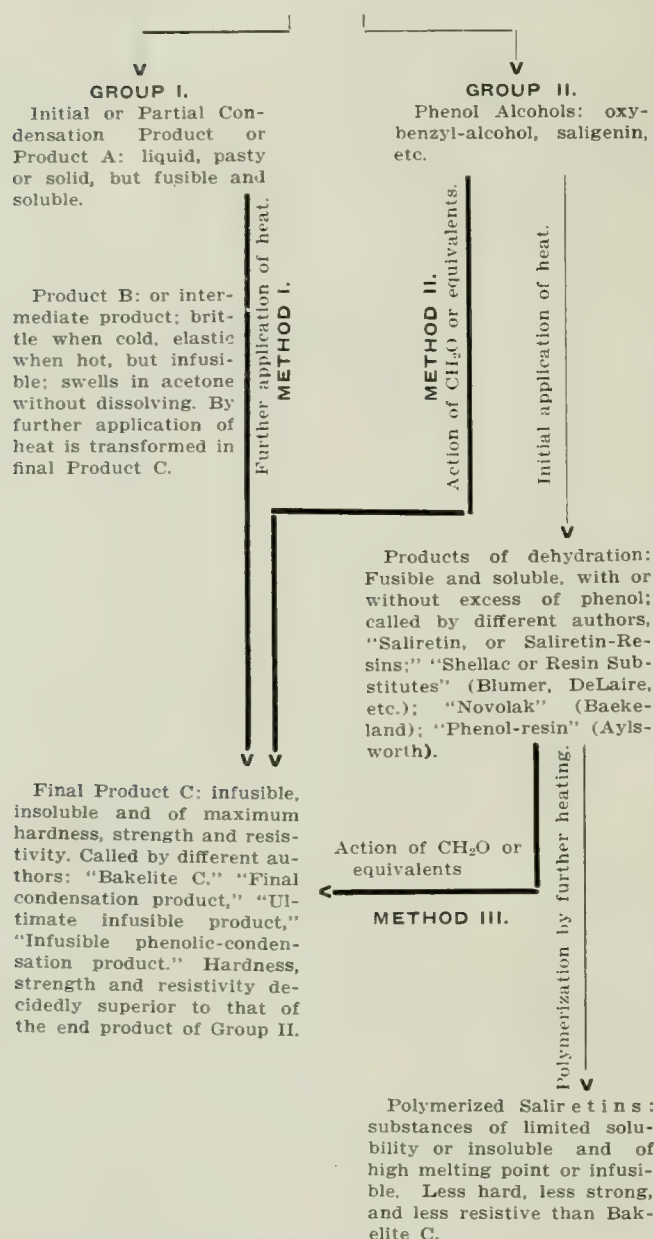
But whenever we succeed in bringing into reaction a sufficient amount of formaldehyde or its equivalent, then a much harder, much stronger and more resistive infusible body than an infusible saliretin will be formed and this body of maximum strength and resistivity is identical with Bakelite C.

If we first produce the pure crystalline phenol alcohol, containing no excess of phenol, for instance crystalline saligenin or oxybenzyl-alcohol, and if we heat it gently, it will simply dehydrate and be transformed into a fusible mass which on cooling solidifies to a resinous product—a fusible saliretin resin. The latter submitted to the further action of heat polymerizes and becomes an infusible, insoluble saliretin. This polymerization is facilitated by the presence of small amounts of catalyzers, for instance, hydrochloric acid. The presence of an excess of phenol retards polymerization, hence the infusibility induced by polymerization will be retarded, and this until in some way or another the excess of phenol has been expelled. The infusible polymerized saliretin obtained by heating phenol alcohols containing no free phenol, or by heating fusible saliretin containing no free phenol, is insoluble in alcohol, but swells in acetone; it softens decidedly on heating, although it is no longer fusible. Longer heating does not harden it further, nor make it more resistive. It is harder, stronger and more resistant to physical and chemical agents than the fusible saliretin from which it is derived; in this respect, it surpasses even more the soluble fusible resins described by Blumer,¹² DeLaire¹², Baekeland¹² and called "phenol resin" by Aylsworth.¹² But even after polymerization or hardening has been carried as far as possible, it is considerably less hard, less strong and less resistant to physical and chemical agents than the polymerization products resulting from the reaction of phenol on a sufficiently larger proportion of formaldehyde or equivalent substances.

¹⁵Austrian Patent 30,844, page 2, lines 17-20.

PHENOL + FORMALDEHYDE (OR EQUIVALENTS) UNDER VARYING REACTING CONDITIONS FORM DIFFERENT

BODIES.



In order to obtain the latter polymerization products of maximum strength, hardness and maximum resistivity, an adequately larger amount of methylen group must be introduced before or during the act of polymerization. The introduction of this methylen group may be accomplished by at least three distinct methods:

First: Reacting directly with a sufficient amount of formaldehyde (or its equivalents) upon phenol.

Second: Reacting with formaldehyde (or its equivalent on phenol alcohol.

Third: Producing a fusible dehydration product of phenol alcohols or saliretin products, then reacting thereon with formaldehyde or its equivalents.

The diagram describes very well all these relations:

FIRST OR DIRECT METHOD.

Direct Action of Phenol on Formaldehyde.—Phenol can be made to react on formaldehyde or its equivalent

at sufficiently high temperature to produce directly an infusible, insoluble polymerization product of maximum strength and hardness (Bakelite C). In this reaction, the main requirement is that a sufficient amount of formaldehyde or its equivalents *should enter into reaction*. For this purpose, it is not necessary nor sufficient that the required amount of formaldehyde be merely present; because some of the formaldehyde may not enter into reaction or be lost during the operation. *The principal requirement is that the formaldehyde should react in sufficient amount on at least a portion of the phenol present*, even if some of the latter remains uncombined in the mass.

By the use of suitable methods, this reaction can be interrupted at its initial stages so as to produce initial or partial condensation products which are temporarily fusible and soluble before further application of heat has changed them. These initial condensation products may be liquid, or pasty, or under specially favorable conditions, for instance by the use of small amounts of some bases, they may be prepared in solid form. At any rate, they are soluble in alcohol and acetone, and the solid variety is fusible. These fusible soluble initial products should not be confounded with the further advanced and intermediate product B, as described in my paper on "The Synthesis, Constitution and Uses of Bakelite,"¹⁶ because the latter is insoluble and infusible, although it has not acquired the maximum hardness and resistivity which further application of heat will bring forth by changing it to condition C.

Further action of heat upon these fusible and soluble initial condensation products will ultimately cause polymerization and produce the final infusible and insoluble product of maximum hardness, maximum strength and maximum chemical resistivity (Bakelite C).

By heating mixtures of phenol and formaldehyde in suitable proportions at sufficiently high temperatures for a sufficiently long time, chemical condensation may take place without the addition of condensing agents or catalytic agents; however, under such unfavorable condition, the action is too slow and too difficult to control for technical purposes.

By the addition of acids or acid salts, the reaction may be hastened to the point of becoming violent. But the presence of acid bodies tends to develop disturbing side-products which lessen the technical value of the final product. Furthermore, in presence of an acid-reacting mixture, whenever there is a sufficient excess of phenol, we do not obtain the infusible, final product, but resins of the fusible saliretin or "shellac substitute" type. Things go quite differently if small amounts of bases are present during the reaction.¹⁷ Small quantities of bases prevent radically the formation of fusible soluble saliretin products (shellac substitutes, Novolak, phenol-resin, etc.) and insure the formation of infusible, insoluble final products, even in presence of a decided excess of phenol. If the phenol be used in excess, it will be found in the final

product as a solid solution. In fact, the excess of phenol may be exaggerated to the point that the final product becomes very flexible or assumes a gelatinous appearance, and swells considerably in certain solvents, like phenol, or alcohol, or acetone, without, however, entering into complete solution. In any case, this free-phenol-containing substance is infusible; in other words, the application of heat can no longer liquefy it, although higher temperatures may char or destroy it.

This behavior of the bases constitutes a radical difference from that of acids or other acid-reacting bodies. Whenever acid-reacting bodies are used in conjunction with an excess of phenol, or an insufficient amount of reacting formaldehyde, which amounts to the same thing, they tend to produce fusible soluble resins, while under exactly the same conditions and with the same proportions of phenol and formaldehyde, small amounts of bases develop *surely* infusible polymerized bodies as ultimate products.

In this method, the bases should be used in relatively moderate amounts; not in molecular proportions, as Manasse and Lederer¹² utilize them for making phenol alcohols, nor as DeLaire¹² employs them to produce the fusible resinous dehydration products of these phenol alcohols. Neither should they be used in such large quantities nor under such conditions as Hentschke¹⁸ recommended for the manufacture of certain antiseptic compounds.

If the amount of base be properly restricted, the reaction proceeds very regularly and remains under easy control. The base acts as an excellent accelerator, both in the condensation and in the polymerization. The use of bases under the above mentioned conditions enables one to carry out the reaction with the utmost uniformity and certainty of results.

At first sight the importance of these seemingly modest facts is not very apparent; no more than the value of the observation that sufficient counterpressure permits quick polymerization at high temperatures without risk of porosity; no more indeed than the realization of the fact that the final product with its great hardness, its strength and other splendid qualities is unelastic and woefully deficient for most industrial purposes where great resistance to shock or vibration is required, and that the incorporation of suitable fibrous materials improves all this by modifying the shattering wave induced by impact. Yet these three main factors have enabled us to harness into technical service an elusive laboratory reaction and have rendered possible the creation of a new industry which is gaining daily in importance.

It has been shown¹⁹ that small amounts of ammonia or amines may be used to good advantage for this purpose. It is a well known fact²⁰ that ammonia or

ammonium salts in presence of formaldehyde produce instantly a corresponding amount of hexamethylenetetramin. In the same way, if any ammonia be added to a mixture of phenol and formaldehyde, a corresponding amount of hexamethylenetetramin is produced which can easily be extracted from the mixture. This fact was confirmed by Lebach, and can easily be ascertained by direct experiment.²¹ It is self-evident that instead of a mixture of phenol and formaldehyde and ammonia, an equivalent amount of hexamethylenetetramin or hexamethylenetetramin-triphenol²² may be used.

So that in the preparation of these bodies, formaldehyde can be replaced by hexamethylenetetramin; this was already published by Lebach in the patent literature as far back as the end of 1907.²³ Whether the phenol mixture be prepared with ammonia or with hexamethylenetetramin, its properties are practically the same, and on heating, both mixtures engender the same product, with the final evolution of ammonia gas.

Whatever be the methods employed, this reaction is strongly exothermic, and heat is set free in the two phases of the reaction: *First*, in the condensation stage, by which the initial product is formed, and water is separated. *Second*, in the final hardening, when the product becomes infusible by polymerization, a considerable disengagement of heat takes place anew. If the substance be heated in thin layers, this self-heating may be unobservable on account of the heat losses; under such conditions, if, however, the mass is thicker or bulkier, and more especially if it be contained in a mold, this self-heating becomes very disturbing and liberates gaseous or volatile products which cannot escape before the mass sets to infusibility; this causes the mass to swell and raise and to become porous, and makes it practically worthless for almost all technical purposes. This was the stumbling block which former investigators tried to avoid by conducting the hardening at very low temperatures, or by the use of suitable solvents which tend to moderate the reaction. This tendency toward foaming exists also if acid-condensing agents are used, or even if no catalytic agents are added at all. The liberated gaseous products may vary according to conditions; in some cases they may consist largely of formaldehyde gas which tends to escape before the reaction is accomplished; if ammonia be used, and more so if hexamethylenetetramin be employed, varying amounts of ammonia gas will be set free.

¹⁰Baekeland, U. S. Patent 942,809.

¹¹Wohl, Ber., 19, 1892; Tollens, Ibid., 17, 653; Carl Goldschmidt, page 29. Bonn, Verlag von Friedrich Cohn, 1903; Cambler, Berchot, Comp. rend., 120, 557.

¹²Lebach, Zelt. angew. chem., 1909, 1600.

¹³The Addition Product of Phenol and Hexamethylenetetramin," see Reilstein, Handb. der Organ. Chem., [3] 2, 651.

¹⁴Knoll, Belgian Patent, loc. cit., and Wetter (Knoll), British patent, loc. cit.

¹⁵Baekeland, U. S. Patent 942,699.

¹⁶"The Synthesis, Constitution, and Uses of Bakelite," loc. cit. See also Baekeland Belgian additional patent 213,657; Baekeland French additional patent 11,628.

¹⁷Baekeland, U. S. Patent 1,038,475.

¹⁸Knoll Belgian patent 204,811, Dec. 31, 1907, and Wetter (Knoll), British patent 28,009, 1907, all owned by the Bakelite Gesellschaft, of Berlin.

¹⁹Aylsworth, Belgian Patent 240,116.

¹⁹Journal of Industrial and Engineering Chemistry, 1, No. 3, 149 (1909).

²⁰See Baekeland, U. S. Patent 942,809.

²¹Loc. cit.

²²Hentschke, D. R. Patent 157,553.

Especially when hexamethylenetetramin is used, the evolution of ammonia is very abundant, and this naturally increases the tendency to foam and to give a porous final product. This tendency to foam becomes pronounced only at temperatures above 50° or 100° C., because at these increasing temperatures the exothermic reaction sets in. It should be noted that temperatures considerably higher than 100° C. are those which are employed in almost all commercial applications of these products, because they allow quick hardening and quick molding. At such high temperatures, polymerization proceeds very rapidly, but the exothermic reaction superinduces a further spontaneous increase of the temperature of the mass, and in this way the defect of foaming is considerably more pronounced.

This tendency to foam makes it of the utmost technical importance whenever high temperatures are employed, for quick commercial work, that the liberation of gaseous or volatile products during the polymerization or hardening process should be opposed by a suitable counter-pressure. The latter may be applied in various ways; for instance, by heating in closed molds or in closed vessels, so that the imprisoned gases develop a suitable counter-pressure; or by heating in a chamber in which air or other gases have first been pumped to a suitable pressure; or by heating in a hydraulic press. In the latter case the first function of the pressure is to counteract the development of gaseous products, while at the same time the mass is given the desired shape in the mold.²⁴

For other applications, life varnishes or lacquer, where the material is applied in thin layers, the use of counter-pressure is not indispensable.

As stated above, the use of ammonia or hexamethylenetetramin increase the tendency to foam. On the other hand, small amounts of fixed alkalis, like caustic soda, act as more powerful accelerators than ammonia or hexamethylenetetramin, without causing the evolution of disturbing ammonia gas or other gases. In this and other respects, the fixed alkalis have decided advantages over ammonia or hexamethylenetetramin, as well as over acid-condensing agents. For instance, they permit rapid hardening at the relatively low temperatures of 70° to 95° C.; furthermore, as soon as the initial solidification has set in, the temperature can be raised quickly to 110° , 120° and 160° C. At these higher temperatures the hardening proceeds with great intensity and without fear that the gas bubbles should cause porosity. If the heating be carried to the hardening temperature before all the water has been first expelled, then the only necessary precaution will be to keep the temperature sufficiently below 100° C. so that there can be no evolution of steam which might cause blisters; but as soon as the mass has been heated long enough at these lower temperatures so that it has solidified sufficiently, the temperature can be raised with impunity above the boiling point of water. As soon as these higher tem-

peratures become available, the polymerization to final hardening advances very rapidly.

For many purposes it is simpler to drive off the water at temperatures below the polymerization temperature, either by drying *in vacuo*, or by drying in a stove at ordinary pressures at moderate temperatures—for instance, 50° C. or below. Such dried material can now be submitted directly to relatively high temperatures without risk of blistering or foaming. This gives us the very best means for rapid hardening, as required by commercial processes. The use of these fixed alkalis has enabled us to carry on hardening and holding at a faster rate than is possible with ammonia or hexamethylenetetramin, or other means, and at the same time to produce molded articles of better heat-resisting qualities, of highest resistivity to solvents, chemicals, and of excellent dielectric properties. For many electrical purposes, the fact that no free ammonia exists in the mass is a further advantage; indeed, this free ammonia is slowly liberated by heat from molded articles and sometimes may play rather disturbing pranks. It has a tendency to corrode brass articles.

SECOND METHOD.

Action of Formaldehyde or Its Equivalents on Phenol Alcohols.—I have described this process in 1908.²⁵

It has been shown that the best results are obtained if the amount of formaldehyde is at least one-sixth of a molecule as calculated to one molecule of phenol alcohol. The same ratio holds good if substances equivalent to formaldehyde or to phenol alcohols are used.

This method has enabled us to gain clearer insight into the relations of all infusible condensation products to the phenol alcohols, and has furnished us the theoretical means for determining the optimum quantities of reacting materials in our technical methods of manufacturing. However, this process is more of theoretical than of practical interest, in as far as the third method accomplishes substantially the same result by starting from the anhydrides of phenol alcohols.

THIRD METHOD.

Action of Formaldehyde or Its Equivalent (Paraform, Hexamethylenetetramin, etc.) on Saliretin-Resins.—The method is another indirect method and consists in first preparing a saliretin-resin of the fusible soluble type, then reacting thereupon with formaldehyde or an equivalent of formaldehyde.²⁶ This method was first published by Lebach at the end of 1907.²⁷

In these patents it is clearly mentioned that paraform and hexamethylenetetramin are equivalent to formaldehyde in the preparation of condensation products. Furthermore, it is described how the condensation products may be prepared in two successive steps by adding the formaldehyde or hexamethylenetetramin, or other equivalents, in two successive quantities. Briefly stated, the process consists in first preparing a

fusible saliretin-resin; to this resin is mixed a second quantity of formaldehyde, paraform or hexamethylenetetramin; this mixture submitted to heat produces the infusible product C. In reality we prepare here in two steps a product which is practically similar to the solid initial condensation product described in the first or direct method. In that method the initial condensation product is obtained more directly by the addition of a sufficient amount of formaldehyde to phenol, in presence of ammonia, or other bases, or by the equivalent use of hexamethylenetetramin or paraform. In the first or direct method the reaction between the phenol and the formaldehyde ensues under elimination of water due to so-called chemical condensation. In the present case, however, a portion of the formaldehyde is first made to react on an excess of phenol, bringing about a corresponding elimination of water by chemical condensation; but in as far as the amount of formaldehyde is insufficient, fusible saliretin-resin is formed. In order to transform the latter into the product C, it is necessary to supply an additional amount of formaldehyde, or some paraform, or hexamethylenetetramin, etc.; hence the necessity of adding a certain amount of those methylen compounds to the fusible saliretin-resin before the mass is submitted to hardening or polymerization by heat. The chemical reaction of the methylen compound on the fusible saliretin-resin is accompanied by the further elimination of water, which can easily be demonstrated by direct experiments.

If hexamethylenetetramin is used, an abundant liberation of ammonia takes place at the same time; but even with the use of the latter, a certain amount of water is liberated by the action of the hexamethylenetetramin on the free phenol contained in the fusible soluble saliretin-resin.

Barring those minor differences in preparation and proportion, the final product C is practically the same as that obtained by the first or direct method as described above.

If hexamethylenetetramin be added to the fusible resin, and heat be applied, the violent exothermic reaction which ensues causes an abundant liberation of ammonia gas. The mass raises like bread, and a hard spongy product is the result. Aylsworth²⁸ utilizes this foaming to prepare this substance in powder form by first producing porous masses of the final condensation product, which can be crushed more easily to a fine powder than if solid lumps of this refractory material have to be pulverized.

In molding processes where high temperatures are needed so as to insure hardening, this violent liberation of ammonia gas can easily be counteracted by suitable counter-pressure. In this case the pressure is not only required for shaping the article, but first and foremost, for avoiding porosity. This can easily be demonstrated by beating the mass in an open mold at the same high temperature as is used in the press; under these conditions direct application of these high

temperatures causes foaming and porosity unless suitable counter-pressure be applied.

It has been claimed that by the use of hexamethylenetetramin in connection with perfectly dry fusible soluble phenol-resin, no water is liberated, which is supposed to be an advantage for certain applications where high dielectric properties are required. However, it should be noted that such fusible soluble phenol-resins all contain considerable amounts of free phenol, and by the action of hexamethylenetetramin on this phenol, water is formed besides the ammonia that is set free.

Moreover, the presence of large quantities of free ammonia is, if anything, more objectionable for certain purposes than the possible presence of small amounts of water.

It is true that free ammonia can be expelled by sufficiently long after-drying of the molded articles, but by the same means it is just as easy to expel the last traces of water. The most striking fact is that there is no serious difficulty in obtaining articles of extremely high dielectric properties, even when starting from raw materials containing considerable amounts of water, provided the manufactured articles be submitted afterward to a drying treatment which can be performed in any suitable drying stove.

It should be noted that almost all molded commercial articles made of phenol-formaldehyde condensation products contain various amounts of fibrous materials, preferably wood pulp or finely divided sawdust. These organic fibrous materials, at the high temperature at which the molding in the hydraulic press takes place (140° to 160° C., or over), begin to liberate variable amounts of water and other products of decomposition, which depress the dielectric properties. This is another reason why all molded articles intended for purposes where high dielectric properties are essential should be submitted to oven-drying after they are molded. Those who are unfamiliar with the technical side of the subject may ask why it would not be simpler to omit altogether the use of fibrous organic materials. They might suggest the use of asbestos. But asbestos has other drawbacks which limit its use. For instance, asbestos is a relatively poor insulator, and the strength imparted by its fibers is not so great as that imparted by vegetable fiber; furthermore, its specific gravity makes the articles compounded therewith very heavy; moreover, any asbestos compositions which have to be machined or milled are very severe on the tools. Another objection is that asbestos compositions do not take the excellent and easy polish which can be easily developed on articles made with wood-fiber compositions, nor do they possess the elasticity and strength of the latter.

It might also be suggested to drop entirely the use of any fibrous material, and to use amorphous or pulverulent fillers. But the technical requirements forbid this. Indeed, the main characteristic of the final phenol-formaldehyde condensation products is that,

although they are exceedingly hard and resistant and have a remarkably high crushing strength, their flexibility and elasticity are very limited. In regard to these latter qualities, they occupy a position between hard rubber and glass. A sudden shock or limited bending shatters them, and this would restrict enormously their technical applications. I found that the shattering wave induced by impact could be considerably modified by the suitable introduction of fibrous or cellular materials, like wood-fiber. This behavior is quite different from that of other plastics, like celluloid or rubber, which lose their best and characteristic qualities by the incorporation of filling materials. The phenol-condensation products, on the contrary, are enormously improved for commercial use if compounded with filling materials, provided the latter be of a fibrous nature; in the latter case they lose their natural brittleness and can stand shock and impact without shattering; they can be rendered flexible and yet maintain all their other excellent properties of high resistivity to physical and chemical agents.

Hence some of the most important industrial applications of these condensation products are precisely those where they are used in conjunction with fibrous bodies; for instance, they serve to impregnate fibrous materials like wood, pulp-board, and to indurate the latter, or to agglutinate firmly loose fibrous substances, like wood-fiber or fine sawdust, which then act as a structural skeleton distributed throughout the indurated mass.

This important technical result is easily demonstrated by comparing the enormous strength and resistance to impact or shock of molding compositions containing wood-fiber with others containing the same amount of structureless filling materials; for example, powdered materials. Compositions made with the latter will be found incomparably more brittle and very much less appropriate, if not entirely unsuitable, for most industrial purposes, more especially for molded articles where great strength is required.

Other important technical results are accomplished with the use of filling materials; for instance, the highest dielectric properties have been rendered possible by the joint favorable action of fibrous material and heat and pressure.

It might be cited here that paper impregnated with these condensation products, and submitted to hardening under heat and pressure, has made it possible to manufacture sheets which show an astonishingly high disruptive test (puncture test), averaging 77,000 volts a. c. on sheets of 1/16 in. thickness, corresponding to 1,230 volts per mil., or about 48,500 volts per millimeter.

Under these favorable conditions the vegetable fiber of the paper is thoroughly impregnated with the condensation product, and the high pressure has excluded the possibility of porosity induced by foaming.

POTASH IN NEBRASKA.

Considerable interest has been aroused in the discovery of soluble potash salts in certain lakes in western Nebraska. The report of their discovery together with samples of the deposits, first came to the Geological Survey from Mr. Carl Modesitt, who has been interested in the possibility of developing the deposits on a commercial basis. One lake was visited by R. B. Dole, of the Geological Survey, who collected from the deposit samples whose potash content has been determined.

Many shallow lakes, 50 to 500 acres in extent, occupy depressions among the sand hills of western Nebraska. At the ordinary stage of water most of the lakes have no surface outlet and some of them are apparently underlain by impervious strata, which prevent the escape of the water by seepage. As a result they form shallow evaporating pans in which large quantities of the alkaline or saline material of the tributary drainage water accumulate and become more or less concentrated.

The lake visited by Mr. Dole, known as Jesse Lake, situated in T. 25 N., R. 46 W., covers about 400 acres and is one of the largest of these bodies of water. It varies in depth from 30 inches to dryness, according to the rainfall and season. The land on the northwest side of the lake is swampy and the water there is not so concentrated in salts, as possibly this is where seepage enters. When the lake was examined in May a strip of the lake shore about 100 feet wide was exposed and the water in the lake was about a foot deep. The shore is brownish-black sticky mud, devoid of vegetation. The lake is entirely surrounded by typical sand hills, and probably a rise of 4 or 5 feet in the water level would be necessary to effect surface run-off.

A partial analysis was made of several samples of water collected at Jesse Lake. The results of these analyses are given below. Nos. 2 and 3 represent water from the lake and No. 4 is a crust from the top of a pit dug on the shore of the lake. No. 5 is mud from a depth of 20 inches on the shore of the lake and No. 6 is from a depth of 10 inches. The determinations were made by A. R. Merz at the Co-operative Laboratory for potash tests. Mackay School of Mines, Reno, Nev., who reports that the salts consist mainly of carbonates but contain also chlorides and sulphates.

POTASH DETERMINATIONS ON SAMPLES FROM JESSE LAKE, NEBR.

	Grams of soluble salts per 100 cc. dried at 105° C.	Percentage of K ₂ O in the total salts.
No. 2.....	2.90	29.91
No. 3.....	3.34	30.00
No. 4.....	47.72	24.97
No. 5.....	1.32	Not determined.
No. 6.....	2.08	Not determined.

These results, so far as they go, confirm those of more complete analyses that have been made by private chemists. The concentration of the total salts in the water is about 3 per cent, nearly the same as ordinary sea water, though the composition of the salts is of course widely different.

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NOTES AND COMMENTS.

Teaching Chemical Analysis.

Those who are engaged in the commercial practice of chemical analysis wonder at times why so many of the young men coming into the laboratories on graduation from college know so little about the details of common technical analysis. Many times, we might nearly say all the time, their methods of analysis, as learned in college, are faulty from the point of accuracy or rapidity.

A possible explanation of this was found in a remark heard at a recent meeting of chemists where the topic of discussion was a certain method employed in the analysis of an industrial product. Many of the men present at this meeting were chemist with from fifteen to twenty years' experience in the analysis of the product under discussion. They had been giving their methods of analysis and indicating some of the time necessary in order to secure accurate results. When they had completed their statements, a young instructor in chemistry from one of our great universities arose and said: "I have not had much practical experience in the analysis of these products, but I would prefer a method where results can be obtained

in from three to four hours, instead of the long time indicated by the previous speakers. There have been some methods of electro-analysis published where such materials as you are discussing can be completely analyzed in three to four hours."

Those present who had had a long experience with the product under discussion knew that electro-analysis was absolutely out of the question for this material, yet this young instructor will not know better than to teach such methods to his students, and the students, of course, will not know better than to attempt to use them.

There has been considerable discussion recently of demanding a code of ethics for chemists practicing their profession. When we demand this, we possibly should reinforce it by demanding that a college instructor should spend at least a few years in the active practice of his profession before he is allowed to impart information to others.

Probably 75 per cent of the instruction in analytical chemistry in our colleges and universities is given by men who have had no experience except their scholastic experience. They know nothing at all about the organization of a technical laboratory or the methods of analysis which are necessary in order to satisfy both the demand for rapidity and accuracy. Their instructors were probably equipped as they. We thus have handed down from generation to generation a mass of misinformation which finally becomes somewhat appalling.

A Code of Ethics.

A committee of the American Institute of Chemical Engineers has recently formulated a code of ethics which they have presented to the members of the institute for their acceptance. The matter of the formulation of such a code of ethics by some body of chemists or chemical engineers has been under discussion for some time. The proposed code of ethics as presented to the Institute is as follows:

Purpose of the Code:

To define the rules of professional conduct and ethics for the members of the Institute.

The Institute expects of its members:

1st. That in all their relations, they shall be guided by the highest principles of honor.

2d. The upholding before the public at all times of the dignity of the chemical profession generally and the reputation of the Institute, protecting its members from misrepresentation.

3d. Personal helpfulness and fraternity between its members and towards the profession generally.

4th. The avoidance and discouragement of sensationalism, exaggeration and unwarranted statements. In making the first publication concerning inventions or other chemical advances, they should not be made through the public press, but through chemical societies and technical publications.

5th. The refusal to undertake for compensation work which he believes will be unprofitable to a client without first advising said client as to the improbability of successful results.

6th. The upholding of the principle that unreasonably low charges for professional work tend towards inferior and unreliable work, especially if such charges are set at a low figure for advertising purposes.

7th. The refusal to lend their names to any questionable enterprise.

8th. Conservatism in all estimates, reports, testimony, etc., especially in connection with the promotion of business enterprises.

9th. That they shall not engage in any occupation which is obviously contrary to law or public welfare.

10th. When a chemical engineer undertakes for others work in connection with which he may make improvements, inventions, plans, designs or other records, he should enter into a written agreement with regard to their ownership; and when it is subsequently found that such an agreement does not cover a point at issue, the following rules shall apply:

a—If a chemical engineer uses information which is not common knowledge or public property, but which he obtains from a client or employer, the results in the form of plans, designs or other records shall not be regarded as his property, but the property of his client or employer.

b—If a chemical engineer uses only his own knowledge or information or data, which by prior publication or otherwise are public property, and obtains no chemical engineering data from a client or employer except performance specifications or routine information, then the results in the form of inventions, plans, designs or other records should be regarded as the property of the engineer and the client or employer should be entitled to their use only in the case for which the engineer was retained.

c—All work and results accomplished by the chemical engineer in the form of inventions, plans, designs or other records, or outside of the field for which a client or employer has retained him, should be regarded as the chemical engineer's property.

d—When a chemical engineer participates in the building of apparatus from designs supplied him by a client, the designs remain the property of the client and should not be duplicated by the engineer or anyone representing him for others without express permission.

e—Chemical engineering data or information which a chemical engineer obtains from his client or employer or which he creates as a result of such information must be considered confidential by the engineer; and while he is justified in using such data or information in his own practice as forming part of his professional experience, its publication without express permission is improper.

f—Designs, data, records and notes made by an employee and referring to his employer's work, should be regarded as his employer's property.

g—A client does not acquire any exclusive right to plans or apparatus made or constructed by a consulting chemical engineer except for the specific case for which they were made.

11th. A chemical engineer cannot honorably accept compensation, financial or otherwise, from more than one interested party, without the consent of all parties; and whether consulting, designing, installing or operating, must not accept compensation directly or indirectly from parties dealing with his client or employer.

When called upon to decide on the use of inventions, apparatus, processes, etc., in which he has a financial interest, he should make his status in the matter clearly understood before engagement.

12th. The chemical engineer should endeavor at all times to give credit for work to those who, so far as his knowledge goes, are the real authors of such work.

13th. Undignified, sensational or misleading advertising should be discouraged.

14th. Contracts made by chemical engineers should be subject to the Code of Ethics.

For the administration of this Code of Ethics, a Committee on Ethics shall be appointed by the president holding office at the time of the adoption of this Code, to consist of five members; one appointed for five years, another for four years, another for three years, another for two years, another for one year, and thereafter, the president then holding office shall appoint one member annually to serve for five years and also fill such vacancies as may occur for the unexpired term. Three of these members shall be over forty-five years of age. The Committee shall elect its own chairman. The Committee on Ethics shall investigate all complaints submitted to them bearing upon the professional conduct of any member, and after a fair opportunity to be heard has been given to the member involved, shall report its findings to the Council, whose action shall be final.

Proposed Code of Ethics of the American Institute of Chemical Engineers.

The following "open letter" regarding the proposed Code of Ethics, printed above, appeared in *Metallurgical & Chemical Engineering*:

Dear Sirs: The fact that other engineering societies have adopted a "Code of Ethics" is not a satisfactory reason why the Institute of Chemical Engineers should adopt one. They may have made a bad mistake in adopting a code, and it would then be no credit to us to follow their example. Let us make our own mistakes, if we are going to make any, and not simply repeat the mistakes of others.

The Institute of Chemical Engineers was intended to be select, to contain only men of prominence and accomplishment in their profession. Its foundation was partly a protest against the indiscriminate character of the membership of the American Chemical Society, and because membership in that society conferred no distinction. Such being the high character of the membership of the Institute, it is unfitting and ill-advised to formulate "rules of conduct" for them, as if they were tyros in the art of being "an honest man and a gentleman."

The adoption of such a code would distinctly lower the dignity and distinction of membership in the Institute. It is, by assumption, unnecessary, because we elect as members only men who by action and achievement have shown themselves to be distinguished gentlemen. To prescribe to such, for example, that they shall "be guided by the highest principles of honor," is as unnecessary as it is silly and ridiculous; indeed, it is a gratuitous insult to every member of the Institute.

I do not hesitate to say, that if any member of the Institute has lost self-respect to such extent that he feels that he, himself, needs such a prescription as that just quoted, to keep him in the path of honor and rectitude, then he should be thoughtful enough to resign from the Institute before he brings discredit upon it. The Institute is not a reformatory.

Neither do I hesitate to say that any member who recognizes that he himself does not need such a prescription, but still would impose it on the Institute "for the benefit of his weaker brothers," is an unmitigated cad, and unfit to direct or influence the proceedings of the Institute.

I sincerely hope that the whole proposition will be voted "down and out" for good; every member who votes for it stultifies himself.

JOS. W. RICHARDS.

Lehigh University, South Bethlehem, Pa.

Lime production in the United States in 1911 amounted to 3,392,915 short tons, a little more than half of which was used in structural material, according to a recent bulletin of the U. S. Geological Survey. The principal uses in the structural field were lime mortars, Portland cement mortars, concrete, gypsum plasters and whitewash.

NIGERIAN TIN: ITS OCCURRENCE AND ORIGIN.

An interesting description of Nigerian Tin, with particular reference to its occurrence and origin, is given by Mr. J. D. Falconer in *Economic Geology*, from which we quote as follows:

The tinfields of northern Nigeria lie mainly in the heart of the Protectorate, on the summit and round the margins of the great central plateau.¹ The tinstone occurs both in placers and in lodes, but up to the present practically all the tinstone which has been exported has been taken from the alluvial deposits. The stream tin had been worked and smelted on a small scale by the natives of Lirue-n-Kano for a lengthy period before the British occupation of Nigeria in 1900, but all that was known of its point of origin was that it was produced somewhere in the pagan and at that time hostile country of Bauchi. It was not indeed until 1902 that a definite effort was made by the Niger Co. to locate the tinstone in Bauchi province, and in 1904 the first mining camp was established on the banks of the Delimi river on the site of what is now Naraguta, the center of the mining industry of western Bauchi. The alluvial tin was thus the first to be discovered, but more recently careful search in the surrounding country has proved the presence of lodes in the vicinity of the placers. Little or no scientific study of these lodes has yet been carried out, but so far as investigation has gone, there would appear to be some slight difference in mineral content between the placers and the lodes, sufficient to suggest the conclusion that the original habitat of the placer tin has not yet been definitely ascertained.

Like most placers the tin-bearing gravels of northern Nigeria are believed to be of comparatively recent age and to date from a period immediately preceding the establishment of the present river system. They are distributed over an area of about 9,000 square miles, mainly in western Bauchi, but extending also into the adjoining provinces of Zaria and Nassarawa. The richer deposits are found in the valleys of western Bauchi where the tinstone has been naturally concentrated by the present streams. Water is available for hand work and for sluicing during the greater part of the year and the ore can be easily and abundantly won from the gravels by the simplest methods. It is in such places only that the work of development has hitherto been attempted, and full credit is due to the Niger Co. for being the first to demonstrate the possibility of working these deposits at a satisfactory profit in the face of many difficulties. Native labor is comparatively scarce, the cost of white supervision is high, and inland transport charges are particularly excessive. The Bauchi tinfields lie at a distance of 150 miles from Loko on the river Benue, the nearest accessible point for steamers and barges, and hitherto the tinstone has had to be carried to the river by porters traveling about

15 miles a day with the ore on their heads in bags of about 60 lbs. weight. It was this difficulty of transport, more than any other, which led in the first instance to the search for and the exploitation of the richer areas only. The poorer alluvials were everywhere neglected and little time was spent in the search for lodes. The absence of railways and even of roads and bridges rendered almost impossible the introduction of heavy machinery by which alone the poorer ground and the lodes could be profitably worked. In spite of all these disadvantages, however, several companies, following the example of the Niger Co., have been able to place quantities of Nigerian tin upon the home market and secure from it a highly satisfactory return. The difficulties of labor and supervision still remain, but the completion of the Baro-Kano railway and of the branch line, now in course of construction, from Zaria into the heart of the tin area will entirely revolutionize the conditions of transport previously existing and put the tinfields into direct communication with the port of Lagos. There is now, therefore, every possibility of the poorer alluvials and of the lodes being easily and profitably worked in the immediate future, and the improved prospects of the industry are now attracting to the country large numbers of prospectors and concessionaires, while a large amount of capital has already been invested in various enterprises of greater or less stability.

With the tinstone in the richest alluvials, there occur in considerable abundance rolled fragments of white and yellow topaz and small pyramidal and octohedral crystals of brown zircon. These two minerals indeed might almost be said to play the part of indicators. Along with them, however, there occur also in the concentrates small quantities of magnetite, ilmenite, rutile, garnet, monazite, and an occasional color of gold, but there is little difficulty in obtaining concentrates sufficiently pure to assay 70 per cent metallic tin. The tinstone itself varies in color from black to ruby or pale yellow and assays about 75 per cent metallic tin. This Nigerian product is said to be one of the best tins imported into Europe and to command a price equal to, if not better than, that of tin from the Straits.

The alluvial deposits are found in close association with extensive masses of alkaline granite which have been injected into the surrounding gneisses and schists, and it was early suggested that the tinstone of the gravels was probably derived from the granite, where it might occur either sporadically as a rock constituent or as stockworks on the margins of the igneous mass. It was not, however, until 1908 that the prospectors of the Niger Co. actually discovered tinstone in the granite, in the neighborhood of Naraguta, but on the summit of the plateau and in the heart of the intrusive mass. At this place the granite shows signs of later movement, of fracturing and fissuring along certain lines and of accompanying pneumatolytic action. The adjoining rock is chloritized and partially mineralized, while the fissures themselves are filled with ore-bearing

¹V. *Geology and Geography of Northern Nigeria*. J. D. Falconer. Macmillan Co., 1911.

pegmatite and veinstuff. The tinstone is associated with various sulphide ores, pyrites, chalcopyrite, tetrahedrite, blende and galena, of all of which little or no trace is to be found in the alluvial deposits. On the other hand topaz and brown zircon appear to be absent from the lode formations yet discovered, and while they are probably also of pneumatolytic origin, their exact mode of occurrence in the granites still remains somewhat doubtful. There is indeed every possibility of lodes and stockworks being yet discovered in the granites, of which tinstone and topaz will be the most conspicuous minerals.

The tinstone in Bauchi province, in and around the plateau and in the Lirue and Ningi Hills to the north, appears everywhere to be associated in this way with masses of uncrushed soda granite. The small quantities of tinstone that have been found in Yola province and on the Kameruns border are probably also of similar origin. Tinstone, however, is also in places found as a constituent of some of the pegmatite dykes which are everywhere abundant amongst the gneisses and schists. These dykes are frequently rich in tourmaline, but, curiously enough, the tourmaline pegmatites, so far as investigation has yet been made, do not carry tinstone. At Eri in Kabba province there are pegmatites in gneiss carrying quartz, muscovite and abundant cassiterite but no tourmaline, and it is probable that many others of similar character may yet be located.

A stanniferous lode four miles in length is reported to have been discovered on the property of the Anglo-Continental Mines Co., in the Jemaa district of Nasarawa province, but the available information concerning it is insufficient to allow of any definite conclusion being drawn as to whether it is a true fissure lode, a stockwork in granite, or a pegmatite dyke in granite or gneiss.

The tin-bearing and tourmaline-bearing pegmatites are very similar in structure and probably belong to the same general period of igneous activity as the larger mass of tourmaline and alkaline granite throughout the Protectorate. It seems probable that the tourmaline granites and pegmatites were formed during an early phase of this igneous period, while the emanations which gave rise to the metallic lodes and the stanniferous pegmatites were characteristic of an entirely distinct and later phase, posterior to the solidification of the larger masses of alkaline granite. It follows, therefore, that in Nigeria the presence of abundant tourmaline in granites and pegmatites is no safe indication of the presence of tinstone in the same neighborhood.

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